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THE DIAGRAM OF STATE OF THE TERNARY SYSTEM $BaO - Al_2O_3 - SiO_2$

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The choice of the three-component system $BaO-Al_2O_3-SiO_2$ as the subject of this investigation was governed by a series of causes. First, the most important of the silicate systems are aluminosilicate compounds due to the great distribution of aluminosilicates throughout the earth's crust and the great variety of industrial silicate products. The relevance of this reason for our choice of the material of our investigation found confirmation in the course of the experimental work, in the earliest stages of which was established the congruence of the melting of mullite. Appropriate corrections were thereupon introduced into the fundamental physico-chemical silicate diagram of $Al_2O_3-SiO_2$.

The second reason was the high refractoriness of the majority of the compounds of the ternary system. This circumstance made the work difficult but at the same time endowed its results with great value. In fact, having developed a laboratory microfurnace of new design, we succeeded not only in investigating the system in question but also in devising a new method for the study of similar refractory systems. It was extremely interesting to compare the diagram with those of previously investigated aluminosilicate systems, as well as with the phase diagram of the system $BaO-B_2O_3-SiO_2$; the detection of complex three-component solid solutions in the system is likewise a matter of great scientific interest.

Of the three binary systems constituting the sides of the ternary diagram, we made a detailed study of the systems $Al_2O_3-SiO_2$ and $BaO-SiO_2$. In the system $Al_2O_3-SiO_2$ is formed the compound frequently encountered in industrial materials – mullite $3Al_2O_3 \cdot 2SiO_2$. This material was first discovered in the composition of porcelain – by Vernadsky [1] and later by Zemyatchensky [2]. The system as a whole was studied in most detail in 1924 by Bowen and Greig [3]. According to the data of these authors, mullite melts with decomposition; it forms a eutectic with silica.

Bauer, Gordon and Moor [4] obtained single crystals of mullite in the form of a boule 2 cm long and 1 cm thick. Fusion of a mixture corresponding to the composition of mullite was carried out in an oxy-hydrogen flame. The authors explain the formation of single crystals of mullite without separation of corundum by the rapid cooling from the temperature of melting to the temperature of crystallization of mullite. This explanation must, however, be rejected, since the crystallizing tendency of corundum is very high and it should certainly crystallize from melts of the mullite composition if the diagram of Bowen and Greig were correct.

The system $BaO-SiO_2$ has been closely investigated by Eskola [5]. The equilibrium relations between the phases were established by the quenching method. The author found a series of compounds in the system: $2BaO \cdot SiO_2$, $BaO \cdot SiO_2$, $2BaO \cdot 3SiO_2$ and $BaO \cdot 2SiO_2$. An equilibrium diagram was constructed on the basis of the investigation. The author indicates the formation of a solid solution between barium disilicate and dibarium trisilicate.

The phase diagram of the system $BaO-Al_2O_3$ has not been studied. Compounds of this system, however, are well known. Barium aluminates have been most completely studied by Toropov [6] who first established the existence of an aluminate of the composition $BaO \cdot 6Al_2O_3$.

The paper by Zimmer and Watts [7] has a direct bearing on the ternary diagram of $BaO-Al_2O_3-SiO_2$. These workers determined the melting point of the system by the cone deformation method. The portion of the diagram adjacent to the $BaO-SiO_2$ side was studied by Thomas [8] by the quenching method in combination with microscopic examination of the crystalline phases. Formation of a ternary solid solution between the barium silicates and celsian was observed, but the results of optical examination did not fully accord with the plotted vertical fields. The natural barium feldspar – celsian – with the composition $BaO \cdot Al_2O_3 \cdot 2SiO_2$ is the sole ternary compound in the system. Various authors have reported triclinic, monoclinic and hexagonal forms of celsian. The synthetic celsian obtained by Ginzberg [9] was a hexagonal variety with the refractive indices $N_g = 1.590$; $N_p = 1.584$; $N_g - N_p = 0.012$.

EXPERIMENTAL

Experimental Furnace. Preliminary tests on specimens from different parts of the diagram of the $BaO-Al_2O_3-SiO_2$ system showed that the greater proportion of the compositions possesses an initial crystallization temperature above 1500°. This circumstance called for an appropriate high-temperature furnace. For a number of reasons laboratory furnaces for temperatures higher than 1500° – Kryptol, graphite tubes, high-frequency – were unsuit-

able for investigations using the quenching method. A new furnace was therefore designed by one of the authors. This was a vacuum micro-furnace with a tungsten resistance giving a temperature of up to 2000°.

The pyrometer for determination of the temperature was graduated against specimens of known melting point in the form of pure metals – platinum, palladium, etc, and also certain compounds.

Furnace of temperatures up to 1600°. The heating element in this furnace was a 0,5 mm diameter wire composed of an alloy of platinum with 20% rhodium. The wire was wound round a sintered corundum, finger-shaped crucible with internal diameter 5 mm and length 100 mm. The crucible was mounted in a metal jacket packed with heat-insulating material. The sample of material to be tested, parcelled in platinum foil, was suspended directly from a platinum-platinorhodium thermocouple. The furnace was constructed at the close of the present investigation and was therefore not used in all cases.

Platinum resistance furnace. This normal annealing furnace, fitted with a device for dropping the sample into the cold, was used for up to 1450°. The temperatures in the two latter furnaces were measured with platinum-platinorhodium thermocouples and with galvanometers. The recordings of the thermocouples were checked by the method of heating of palladium, gold or silver wires.

Synthesis of specimens

The following starting materials were used: 1) silica in the form of a fine powder prepared from rock crystal. After heating, rapid cooling in water and pulverization in a steel mortar, the rock crystal was treated with dilute hydrochloric acid, washed with water and dried. Final pulverization was effected in an agate mortar. The product contained 99,90% SiO_2; 2) calcined alumina with a total content of impurities of 0,2%; 3) barium carbonate, chemically pure, containing 99.98% $BaCO_3$.

Preparation of homogeneous samples by fusion of mixtures of the components in platinum crucibles was ruled out due to the high melting points. Homogenization of the samples was therefore effected by fusion in an electric arc. Precisely weighed amounts of the starting materials (weighed on an analytical balance) were thoroughly mixed by co-grinding in a mortar, they were moistened with dextrin solution and shaped into 4-5 mm diameter rods with the help of a glass tube. After drying, the specimens were fused in an electric arc.

Method of investigation

The best method of studying the phase equilibria is the quenching method. It is difficult to employ, however, when crystallization of the melt takes place very quickly and the vitreous state cannot be stabilized. For the portions with high liquidus temperatures and a high rate of crystallization, the diagrams were therefore plotted from the melting points.

The melting point, determined by any desired method, is not always the true liquidus temperature. Only in the case of chemical compounds and of eutectic points does the melting point coincide with the liquidus temperature. Nevertheless if the melting points of a series of points are determined, then the general course of the liquidus curve can be revealed. The occurrence of an inflexion on such a curve indicates the existence of a eutectic or chemical compound at the turning point. Melting-points were determined by a method specially developed for use with the micro-furnace.

Finally, for establishment of the primary phase in samples with a high liquidus temperature and a high speed of crystallization the following method was employed. The sample in the form of a small chip was placed in the micro-furnace as for determination of the melting point. Heating was applied until the sample melted, and the temperature was held for 0,5-2 min. The current was switched off and air was passed through the furnace to accelerate cooling, the container was quickly removed and the sample blown with air. If two crystalline phases were formed, as could be established by observation under the microscope, the experiment was repeated at higher temperatures until only one crystalline phase was obtained.

Examinations under the microscope were made for the most part on immersed preparations and rarely on polished sections. In some cases the data were supplemented by X-ray diagrams. The indices of refraction of the glasses were measured by the immersion method. Densities of the glassy products were determined with a pyknometer. In this case the glasses were taken in the form of chips and not in the pulverized state. The chemical stability of the glasses obtained in the system was determined in the following manner. Two glassy pellets (obtained in the arc) were measured along three mutually perpendicular directions and their surface was calculated. The pellets were charged into an exact volume (50 ml) of 0,005 N hydrochloric acid, and the solution was heated 30 minutes on a water bath and left at room temperature for 24 hours. The excess of acid was then titrated with alkali solution. The amount of acid combined per 100 mm^2 of specimen surface gave an approximate indication of its relative chemical stability.

Experimental Results

The study of the diagram was started from the fields bordering upon the binary systems. In the field round the binary system $BaO-SiO_2$ the boundary between the zones of stability of barium silicates followed a course in conformity with this system. The question of the position of the boundary between the fields of dibarium silicate and barium oxide remained unsettled.

In the region of the diagram from 75 to 93% barium oxide the melting points of a series of compositions were determined. The melting point of dibarium silicate was found to be 1730°. It gives a eutectic with barium oxide. The composition of the eutectic is: BaO 87% and SiO_2 13%; m.p. 1600°. The position of the fields on the $BaO-Al_2O_3$ side is likewise not inconsistent with the data for this system. Up to recently, however, the phase diagram itself of the system $BaO-Al_2O_3$ had not been established and it was studied in connection with the present investigation [10].

Finally, in the course of investigation of the field bordering on the $Al_2O_3-SiO_2$ side, the arrangement of the boundary curve between the mullite and corundum fields was observed to deviate from the position according to the generally accepted phase diagram of the system $Al_2O_3-SiO_2$. The occurrence of primary crystallization of mullite was observed in the field directly bordering upon the figurative point of its composition, whereas according to the old diagram [3] mullite melts with decomposition. This observation prompted a special investigation of the binary system in the portion with a high content of alumina [11].

Structure of the diagram of $BaO-Al_2O_3-SiO_2$

In the study of the ternary diagram 305 compositions were synthesized and subjected to test. The general form of the ternary diagram in percentages by weight with the plotted isotherms is shown in Figure 1. The whole diagram comprises 13 fields of stability of the following phases:

1. Tridymite (SiO_2)
2. Mullite ($3Al_2O_3 \cdot 2SiO_2$)
3. Corundum (Al_2O_3)
4. Barium hexaaluminate ($BaO \cdot 6Al_2O_3$)
5. Barium monoaluminate ($BaO \cdot Al_2O_3$)
6. Tribarium aluminate ($3BaO \cdot Al_2O_3$)
7. Barium oxide (BaO)
8. Dibarium silicate ($2BaO \cdot SiO_2$)
9. Monobarium silicate ($BaO \cdot SiO_2$)
10. Ternary solid solution ($2BaO \cdot 3SiO_2 - BaO \cdot 2SiO_2 - BaO \cdot Al_2O_3 \cdot 2SiO_2$)
11. Barium disilicate ($BaO \cdot 2SiO_2$)
12. Celsian ($BaO \cdot Al_2O_3 \cdot 2SiO_2$)
13. Solid solution of an incongruent composition of composition ($3BaO \cdot 3Al_2O_3 \cdot 2SiO_2$)

In the field of the triangle was established the zone of primary crystallization of a hitherto unknown phase of variable composition ($3BaO \cdot 3Al_2O_3 \cdot 2SiO_2$). As we see from the diagram, the system contains two series of solid solutions, one of which is ternary and therefore a rarity among silicate systems. On the diagram are three (actual) binary systems: celsian-corundum; celsian-dibarium silicate; celsian-monobarium silicate. The fields of primary crystallization form 24 boundary curves. There are 11 binary eutectic points and 13 invariant points of which 4 are eutectic and 9 reaction points. The composition and temperature of the invariant points are given in Table 1. A part of the field of the triangle is occupied by compositions formed with sufficiently rapid cooling of the glass.

In Fig. 2 are plotted the curves corresponding to glasses with a constant refractive index; Fig. 3 relates to glasses of constant density; and Fig. 4 to glasses with constant chemical stability toward highly diluted hydrochloric acid. The boundaries between the fields of the region bordering upon the barium oxide corner were determined on the basis of the melting points and the course of the isotherms, and therefore the boundaries are indicated by broken lines. Determination of the primary phases by microscopic observation was unreliable due to the great velocity of crystallization and also to their chemical instability. The field of celsian and its figurative point occupy a central position in the triangle. Celsian crystallizes in the hexagonal modification described by Ginzberg [9]. Particularly good hexagonal plates were separated close to the boundaries of the field.

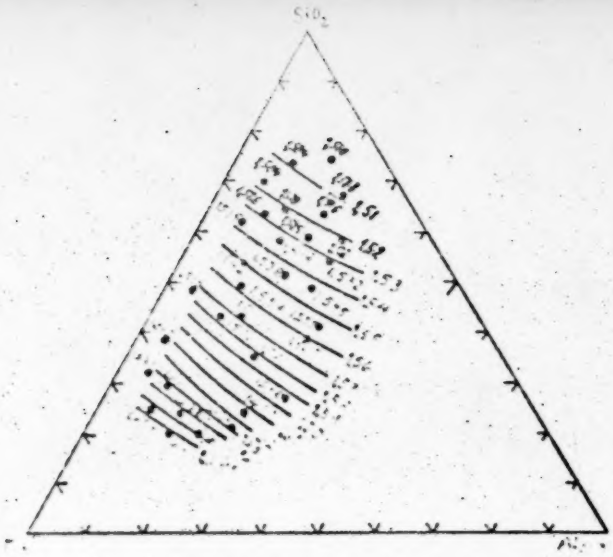

Fig. 2. Light refraction of glasses of the system $BaO-Al_2O_3-SiO_2$.

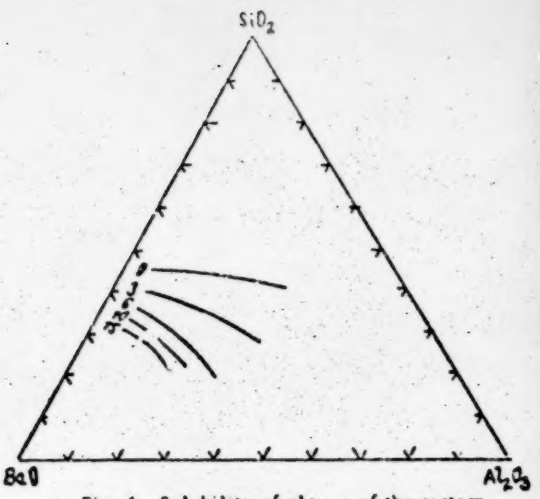

Fig. 4. Solubility of glasses of the system $BaO-Al_2O_3-SiO_2$ in dilute HCl (for the significance of the values see text).

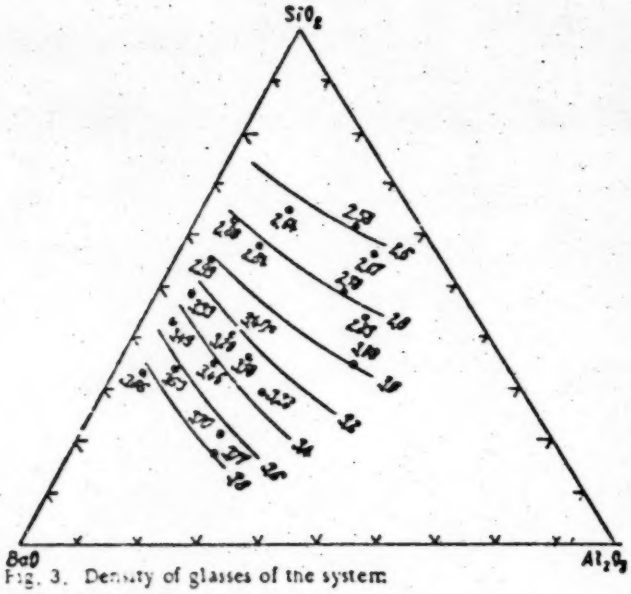

Fig. 3. Density of glasses of the system $BaO-Al_2O_3-SiO_2$

A new ternary compound $3BaO \cdot 3Al_2O_3 \cdot 2SiO_2$.

Already during the preliminary study of the field of the triangle on the portion between the fields of celsian and barium monoaluminate there was observed crystallization of a previously unknown phase with variable optical constants, differing from all known compounds of the components of the system; this pointed to the presence of a solid solution. The clarification of the question as to which compounds form this solution proved to be extremely difficult. Attempts to isolate the new phase without admixture with other crystalline phases during complete crystallization did not lead to the desired result: it was always accompanied by other crystals.

Detailed study of many compositions from this region by the quenching method enables sufficiently accurate determination of its boundaries and of the character of the liquidus surface. The field of primary crystallization of the given phase takes the form of an elongated band whose maximum width occurs with a 3% change of concentration. A temperature peak at the liquidus surface could not be established, the temperature dropped uniformly from the corner of the field with the maximum content of alumina in the direction of the region of celsian and dibarium silicate. All these data, as well as the general position of the field among the other fields of the diagram indicate that not one of the known compounds of the system enters into the solid solution in question. There remained one possibility: the components of this solid solution (or at least one of them) are incongruent compounds. This hypothesis was supported by the direction of rise of the liquidus surface. The simplest formula in the assumed direction was $3BaO \cdot 3Al_2O_3 \cdot 2SiO_2$. A specimen of this composition when kept at 1050° for an hour crystallized in the form of one phase similar in crystalline structure to the solid solution concerned; it possessed the lowest optical constants: $Ng = 1.624$; $Np = 1.615$, $Ng - Np = 0.009$. Quenching of this specimen from 1600° only gave a grain of barium monoaluminate and a glass, which is fully understandable since the investigated composition lies in the region of primary crystallization of the monoaluminate. The temperature below which only the new phase crystallized and above which a glass remained was found to be 1500°.

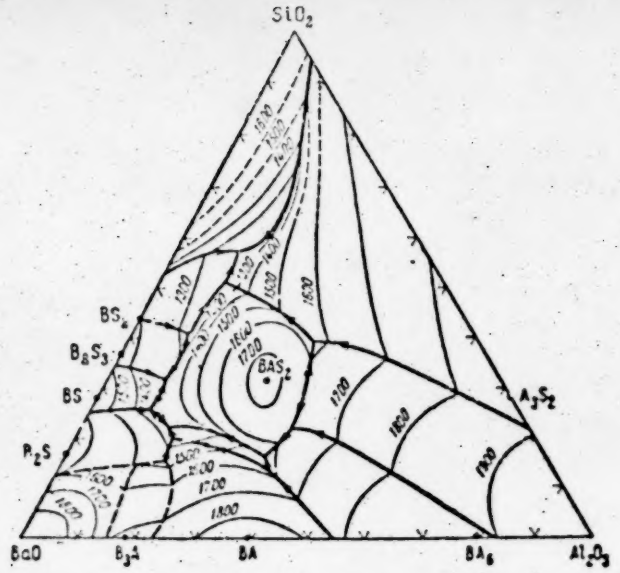

Fig. 1. Phase diagram of the system $BaO - Al_2O_3 - SiO_2$.

Fig. 6. Photomicrograph of section of the compound $3BaO - 3Al_2O_3 - 2SiO_2$ (crossed Nicols X 320).

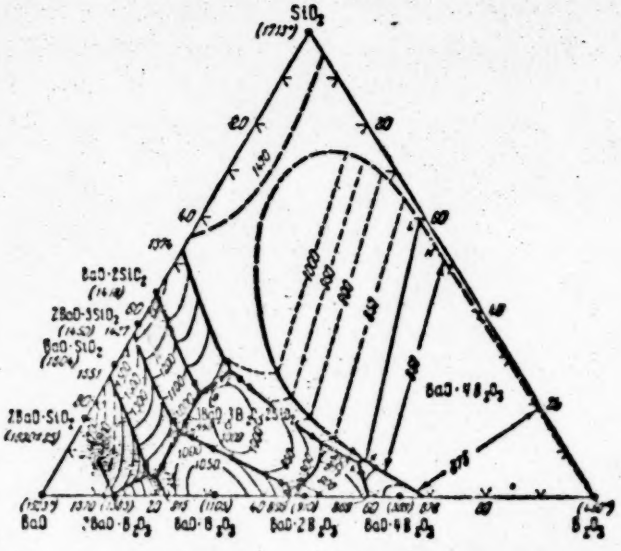

Fig 5. Phase diagram of the system $BaO - B_2O_3 - SiO_2$.

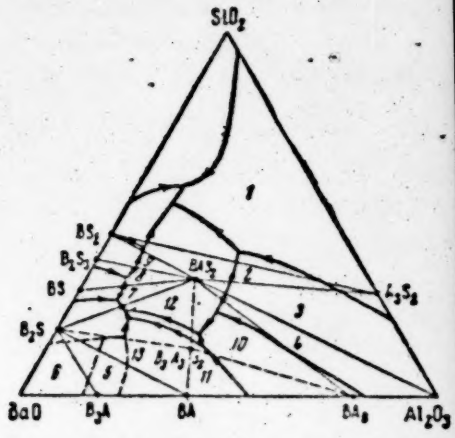

Fig. 7. Phase triangles of the diagram of $BaO - Al_2O_3 - SiO_2$: 1) $SiO_2 - BS_2 - A_2S_3$; 2) $BAS_2 - BS_2 - A_3S_2$; 3) $BAS_2 - A_3S_2 - Al_2O_3$; 4) $BAS_2 - Al_2O_3 - BA_6$; 5) $BS_2 - B_3A - BA$; 6) $B_2S - BaO - B_3A$; 7) $BAS_2 - BS - B_2S$; 8) $BAS_2 - B_2S_3 - BS$; 9) $BAS_2 - BS_2 - B_2S_3$; 10) $BAS_2 - BA_6 - B_3A_3S_2$; 11) $BA - BA_6 - B_3A_3S_2$; 12) $BAS_2 - B_2S - B_3A_3S_2$; 13) $B_2S - BA - B_3A_3S_2$.

TABLE 1

Invariant points of the system $BaO-Al_2O_3-SiO_2$

Points	Phases	Process	Composition						Temperature °C
			wt. %			mol %			
			BaO	Al_2O_3	SiO_2	BaO	Al_2O_3	SiO_2	
1	Al_2O_3 + $3Al_2O_3 \cdot 2SiO_2$ + $BaO \cdot Al_2O_3 \cdot 2SiO_2$ + liquid	Reaction	28	32	40	15.7	27	57.3	15
2	Al_2O_3 + $BaO \cdot 6Al_2O_3$ + $BaO \cdot Al_2O_3 \cdot 2SiO_2$ + liquid	Reaction	41	37	22	26.9	36.4	36.7	16
3	Sol. soln. + $BaO \cdot 6Al_2O_3$ + $BaO \cdot Al_2O_3 \cdot 2SiO_2$ + liquid	Reaction	48.5	35	16.5	33.8	36.8	29.4	15
4	Sol. soln. + $2BaO \cdot SiO_2$ + $BaO \cdot Al_2O_3 \cdot 2SiO_2$ + liquid	Eutectic	63	14.5	22.5	44.3	15.3	40.4	13
5	$2BaO \cdot SiO_2$ + $BaO \cdot SiO_2$ + $BaO \cdot Al_2O_3 \cdot 2SiO_2$ + liquid	Eutectic	64	10	26	44	10.3	45.7	13
6	$BaO \cdot SiO_2$ + Sol. soln. + $BaO \cdot Al_2O_3 \cdot 2SiO_2$ + liquid	Eutectic	58	10	32	37.5	9.8	52.7	13
7	Sol. soln. + $BaO \cdot 2SiO_2$ + $BaO \cdot Al_2O_3 \cdot 2SiO_2$ + liquid	Reaction	49	10	41	28	8.9	62.1	12
8	$BaO \cdot 2SiO_2$ + $3Al_2O_3 \cdot 2SiO_2$ + $BaO \cdot Al_2O_3 \cdot 2SiO_2$ + liquid	Reaction	37	11	52	19.8	9	71.2	12
9	$BaO \cdot 2SiO_2$ + SiO_2 + $3Al_2O_3 \cdot 2SiO_2$ + liquid	Eutectic	32	11	57	16.4	8.6	75	12
10	Sol. soln. + $BaO \cdot 6Al_2O_3$ + $BaO \cdot Al_2O_3$ + liquid	Reaction	49	37	14	34.8	39.7	25.5	1
11	Sol. soln + $BaO \cdot Al_2O_3$ + $2BaO \cdot SiO_2$ + liquid	Reaction	63	16.5	20.5	45	17.7	37.3	13
12	$BaO \cdot Al_2O_3$ + $3BaO \cdot Al_2O_3$ + $2BaO \cdot SiO_2$ + liquid	Reaction	66	18	16	49.3	20.2	30.5	1
13	$3BaO \cdot Al_2O_3$ + BaO + $2BaO \cdot SiO_2$ + liquid	Reaction	72	13	15	55.3	15.1	29.6	1
PAS$_2$	$BaO \cdot Al_2O_3 \cdot 2SiO_2$ + liquid	Melt	41.1	27.2	31.7	25	25	50	1

All these results enable us to conclude that the substance in question is a new barium aluminosilicate of the co position on $3BaO \cdot 3Al_2O_3 \cdot 2SiO_2$ (BaO – 52, Al_2O_3 – 34.50 and SiO_2 – 13.5 wt.-%), which at 1550° melts with decomposi to into the monoaluminate $BaO \cdot Al_2O_3$ and a liquid. Here it is interesting to note that in the ternary system $BaO-B_2O_3-S$ was recently established the formation of a compound of similar stoichiometry $3BaO \cdot 3B_2O_3 \cdot 2SiO_2$ [9,12]. The diagram on which can be seen the position of the field of crystallization of this compound is shown in Figure 5.

In the system in question the formation also takes place of a ternary solid solution occupying a position analog to the position of the ternary solid solution in our system; on the diagram it is shown in the form of a shaded area. region of the possible existence of the composition of the other incongruent compound should be ascertainable by start first, from the position of the field of stability of the solid solution and, second from the change of refractive inde The light refraction of the solid solution increased with the distance from the point of the 3:3:2 composition in the direction of the $BaO-SiO_2$ side of the triangle. Attempts to find the other ternary compound in the indicated directio were, however, unsuccessful. The probable second component of the solid solution may be regarded as barium meta-silicate, judging by the character of the arrangement of the field and the change in the refractive index of the solid solution.

A photomicrograph of a polished section (Fig. 6.) illustrates the crystal form of this new phase; it is made up of elongated prisms with right extinction interlacing and mutually intergrowing at various angles. The interstices between the crystals are filled with glass and with secondary segregations of celsian. The light refraction fluctuates within the following limits: Ng = 1.624 – 1.644 and Np = 1.615 – 1.632.

TABLE 2

Sequence of separation of crystalline phases in the region of the solid solution of the ternary system $BaO-Al_2O_3-SiO_2$

Composition in wt. %			Conditions		Phases
BaO	Al_2O_3	SiO_2	Duration	Temp. in deg. C.	
1	2	3	4	5	6
62.5	15	22.5	2 hours, 30 minutes	1350	Glass
			2 hours, 30 minutes	1300	Glass + BAS_2
			1 hour, 40 minutes	1200	Glass + BAS_2 + B_2S
63	16	21	1 hour,	1350	Glass
			1 hour	1300	Glass + B_2S
			1 hour	1200	Glass + B_2S + BAS_2
60	17.5	22.5	2 hours	1350	Glass
			1 hour, 15 minutes	1300	Glass + Sol. soln.
			2 hours	1250	Glass + solid solution + BAS_2
62.5	17.5	20	2 hours	1360	Glass
			2 hours	1300	Glass + BA + solid solution
62.5	20	17.5	20 minutes	1450	Glass
			30 minutes	1400	Glass + BA
			40 minutes	1250	Glass + BA + B_2S
60	20	20	60 minutes	1400	Glass
			2 hours	1360	Glass + solid solution
			1 hour, 30 minutes	1200	Glass + solid solution + B_2S
57	20	23	30 minutes	1430	Glass
			30 minutes	1350	Glass + BAS_2
			3 hours, 30 minutes	1300	Glass + BAS_2 + solid solution
60	22.5	17.5	15 minutes	1600	Glass
			20 minutes	1380	Glass + BA
			2 hours, 15 minutes	1350	Glass + BA + solid solution
54.7	24	21.3	30 minutes	1450	Glass
			30 minutes	1400	Glass + BAS_2
			20 minutes	1350	Glass + BAS_2 + solid solution
55	25	20	40 minutes	1420	Glass
			1 hour, 30 minutes	1380	Glass + solid solution
			6 hours	1250	Solid solution + BAS_2
57.5	25	17.5	15 minutes	1600	Glass
			30 minutes	1550	Glass + BA
			30 minutes	1400	Glass + BA + solid solution
52	28	20	30 minutes	1500	Glass
			30 minutes	1470	Glass + BAS_2
			20 minutes	1400	Glass + BAS_2 + solid solution
53	30	17	30 minutes	1550	Glass
			30 minutes	1530	Glass + BA
			30 minutes	1500	Glass + BA + solid solution
48.7	32.3	19	15 minutes	1600	Glass
			30 minutes	1550	Glass + BAS_2
			10 minutes	1490	Glass + BAS_2 + solid solution
50	33	17	20 minutes	1600	Glass
			10 minutes	1560	Glass + solid solution
			10 minutes	1530	Glass + solid solution + BAS_2
50	35	15	30 minutes	1600	Glass
			30 minutes	1550	Glass + solid solution
			25 minutes	1500	Glass + solid solution + BAS_2
51.9	34.6	13.5	15 minutes	1600	Glass + BA
			40 minutes	1050	Solid solution
47.5	35	17.5	15 minutes	1600	Glass
			40 minutes	1550	Glass + BAS_2
			60 minutes	1500	Glass + BAS_2 + BA_6
45.5	37	17.5	15 minutes	1600	Glass + BA_6 + BAS_2

(continued on following page)

TABLE 2 (cont.)

1	2	3	4	5	6
45	38	16	15 minutes	1600	Glass + BA_2
			40 minutes	1550	Glass + BA_6 + solid solution
45.5	36.5	18	15 minutes	1600	Glass
			40 minutes	1550	Glass + solid solution
			60 minutes	1500	Glass + solid solution + BA_6 + BAS_2
47	40	13	20 minutes	1600	Glass + BA_6
			40 minutes	1550	Glass + BA_6 + solid solution
49	37	14	15 minutes	1600	Glass + BA_6
			40 minutes	1550	Glass + BA_6 + solid solution
50	37	13	15 minutes	1600	Glass + solid solution + BA

The course of crystallization in the region of this solution and of the adjacent fields is clarified by the data of Table 2, in which the sequence of separation of the crystalline phases is shown. The boundary with the monoaluminate field is incongruent in character; the boundary with the celsian field is eutectic in character. The division of the whole diagram into phase triangles is shown in Figure 7. This enables speedy establishment of the final products of crystallization of the various compositions in the system. Triangle 9 is a two-phase one since one of the sides represents solid solutions. Triangles 10 to 13 are distinguished in the diagram by a broken line because one of the phases ($B_3A_3S_2$) melts with decomposition.

Technological Application

Prominent in the region of glassy compositions of the diagram is the zone located in the "valley" bordering on the curve between the $BaO\text{-}2SiO_2$ and $3Al_2O_3\text{-}2SiO_2$ fields (Fig. 1), which may present interest for glass technology. The glasses of this zone, as far as one can judge from the data obtained in the present investigation, combine valuable industrial and technical qualities. They are relatively low-melting (liquidus temperature approx. 1200°) and are difficultly crystallizable, and they have lower silica contents and higher chemical stability. All these characteristics suggest the possibility of obtaining valuable technical glasses by blending the components of the system in the indicated region with other oxides.

The high quality of celsian ceramic products is well known. The recommended compositions of such products [13] are extremely interesting. They were derived from technical tests of various compositions on the basis of the oxides of the system in question: BaO from 31 to 51%; Al_2O_3 from 17 to 37%; SiO_2 from 22 to 42%. It appears that these values precisely mark the region of the diagram in which the whole of the field of stability of celsian is located. The application of the diagram to the development of recipes and procedures for firing may lead to further advances in the improvement of the quality of celsian products.

SUMMARY

1. An investigation established the congruence of melting of mullite, and the appropriate corrections were introduced into the phase diagram of the system $Al_2O_3-SiO_2$.

2. The phase diagram of the system $BaO-Al_2O_3-SiO_2$ was studied; it comprises 13 fields of stability of the various phases.

3. In the system is formed a ternary solid solution between the silicates $2BaO\cdot3SiO_2$ and $BaO\cdot2SiO_2$ and the aluminosilicate $BaO\cdot Al_2O_3\cdot2SiO_2$.

4. Formation of a previously unknown aluminosilicate of the composition $3BaO\cdot3Al_2O_3\cdot2SiO_2$ was observed. This compound melts with decomposition into the monoaluminate $BaO\cdot Al_2O_3$ and a liquid.

5. A new high-temperature micro-furnace was designed.

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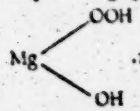
STUDY OF SYSTEMS CONTAINING CONCENTRATED HYDROGEN PEROXIDE

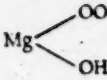
COMMUNICATION 6. 9 AND 20° ISOTHERMS OF THE TERNARY SYSTEM $Mg(OH)_2 - H_2O_2 - H_2O$

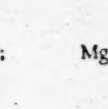
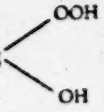
S. Z. Makarov and I. I. Volnov

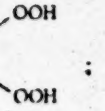
Products known by the names of "heavy", "semiheavy", "light" magnesium peroxide, containing from 12 to 50% MgO_2, are supplied by the chemical industry for pharmaceutical purposes, as an activator in the vulcanization of synthetic rubber, and as a bleaching agent in the textile industry. By a preparative method (in the main by interaction of magnesia with hydrogen peroxide) various authors [1-7] have obtained 19 magnesium products containing MgO_2 which are regarded as a mixture of MgO and MgO_2, $Mg(OH)_2$ and MgO_2, as molecular compounds of MgO and H_2O_2, as basic hydroperoxides of the gross composition  $\cdot xH_2O$, and as products of sorption of H_2O_2 on magnesia. The lack of systematic investigations based upon the methods of physicochemical analysis is a main cause of the discrepancies in the results obtained.

For determination of the character of the possible forms of the peroxy compounds of magnesium, we plotted on the Gibbs phase diagram of $MgO - H_2O - 0.5O_2$ (Fig. 1) the compositions of 19 products mentioned in the literature, the figurative points of the main compounds involving H_2O, H_2O_2, MgO, MgO_2 and $Mg(OH)_2$ and of the hypothetical compounds $2MgO \cdot MgO_2$ and $MgO \cdot 4MgO_2$ for which the existence of hydrates may be possible.

Examination of the diagram shows that of the 19 magnesium compounds reported in the literature, specific chemical compounds can only be associated with the figurative points corresponding to the compositions:

MgO_2; $MgO_2 \cdot 2H_2O$ or $Mg(OH)_2 \cdot H_2O_2$ or  $\cdot H_2O$;

$MgO_2 \cdot 1.5H_2O$ or  $\cdot H_2O$; $MgO_2 \cdot H_2O$ or $MgO \cdot H_2O_2$ or  ;

 ;

the remaining products may be regarded as mixtures.

The best method of approaching the problem of the composition of the products possible as a result of interaction of MgO or $Mg(OH)_2$ with H_2O_2 solutions will evidently be a systematic study of the equilibria in the ternary system $Mg(OH)_2 - H_2O_2 - H_2O$ by the solubility method and by a special physicochemical study of the solid phases of this system.

EXPERIMENTAL

Procedure. In the investigation of the system $Mg(OH)_2 - H_2O_2 - H_2O$ we used solutions of chemically pure H_2O_2 (without inhibitor) of 1.5 to 97% concentration and chemically pure magnesia (Merck). According to the label the MgO contained the following impurities: Cl' 0.00%; PO_4''' 0.0006%, SO_4'' 0.00%, Pb'' 0.001%, Fe''' 0.0005%.

The magnesia was calcined at 800° to constant weight for complete elimination of CO_2 since $MgCO_3$ dissociates in the 600-800° range; it was then slaked by Feitknecht's method [8] for 48 hours with a hundredfold excess of distilled water previously thoroughly boiled with stirring and periodic heating to 90°. Analysis showed that slaking was complete since after drying to constant weight at 115° the product contained 30.87% H_2O [$Mg(OH)_2$ contains 30.86% H_2O]. Water of constitution was determined by calcining at 500-550° since $Mg(OH)_2$ dissociates completely at 410°. After slaking, the liquid phase was decanted. The suspension of $Mg(OH)_2$ contained on the average 80% H_2O. The solubility vessel containing the $Mg(OH)_2$ suspension was placed

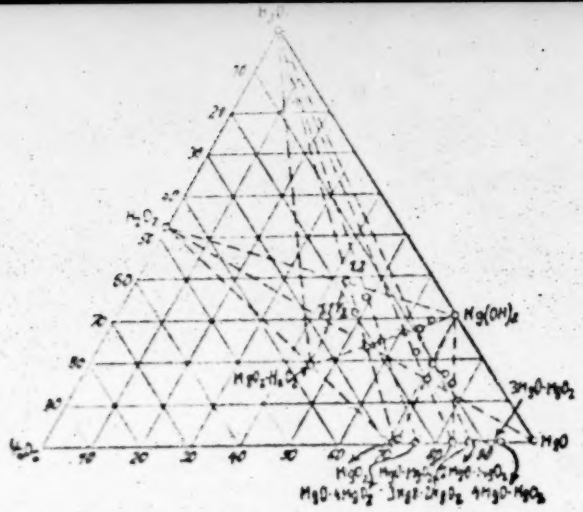


Fig. 1. Compositions of peroxy compounds of magnesium according to literature data in the Gibbs phase diagram

In an ice-filled cryostat and after cooling, a definite volume of H_2O_2 solution of increasing concentration was added for each of the "points" to be determined in such a manner that the excess of H_2O_2 ranged from 1.5 to 150 of the stoichiometric amount. The time established for attainment of equilibrium did not exceed 3 hours. The composition of the solid phases was established by the residue method (plotting on the Gibbs phase diagram the analytical data for the liquid phases and residues). The active oxygen in the residues was determined by titration with 0.1 N $KMnO_4$, and the Mg ion in the form of $Mg_2P_2O_7$. In the liquid phase the active oxygen was likewise determined by titration with 0.1 N $KMnO_4$, but the Mg ion, due to the poor solubility of $Mg(OH)_2$ – of the order of 10^{-4} mole/liter was determined colorimetrically, after complete decomposition of the H_2O_2, with the help of titanium yellow indicator using Kolthoff's method [9] and a FEK-1 electrophotocolorimeter.

Solubility data for the 0 ° isotherm of the system $Mg(OH)_2 - H_2O_2 - H_2O$: The solubility data for the 0 ° isotherm of the system $Mg(OH)_2 - H_2O_2 - H_2O$ are presented in Table 1 and Figure 2.

As we see from Fig. 2, at least 3 solid phases are stable at 0 deg: $Mg(OH)_2$ in the range from 0 to 1.5 % H_2O_2; $MgO_2 \cdot H_2O$ in the range from 1.5 to 62% H_2O_2 and MgO; and $MgO_2 \cdot \frac{1}{2} H_2O$ in the range from 62 to 97% H_2O_2. Anhydrous magnesium peroxide is not formed at the temperature in question.

TABLE 1

Point Number	Liquid Phase		Residue		Solid phase
	wt. % MgO	wt. % $1/2\ O_2$	wt. %	wt. % $1/2\ O_2$	
1	0.002	—	—	—	$Mg(OH)_2$
15	0.05	0.43	25.48	8.50	$Mg(OH)_2$ + $MgO_2 \cdot H_2O$
8	0.02	0.62	21.12	8.48	$MgO_2 \cdot H_2O$
9	—	6.02	19.61	11.60	ditto
16	0.01	6.37	20.86	13.51	ditto
7	0.02	9.04	—	—	ditto
3	0.03	15.47	—	—	
20	0.10	16.02	25.70	20.60	ditto
12	0.14	27.83	16.82	26.22	ditto
11	0.13	28.45	16.20	26.66	ditto
5	0.10	33.61	20.10	30.48	$MgO_2 \cdot 0.5H_2O_2$
13	0.04	38.99	14.63	35.10	ditto
17	—	43.35	14.12	39.54	ditto
14	—	44.45	16.67	38.36	ditto
19	—	45.06	25.73	36.11	ditto
18	—	45.25	22.49	36.92	ditto

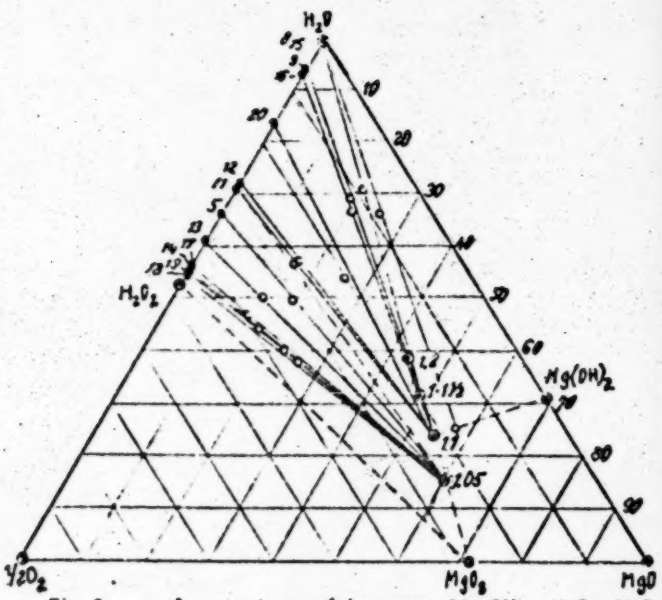


Fig. 2. ° isotherm of the system $Mg(OH)_2 - H_2O_2 - H_2O$ in triangular coordinates.

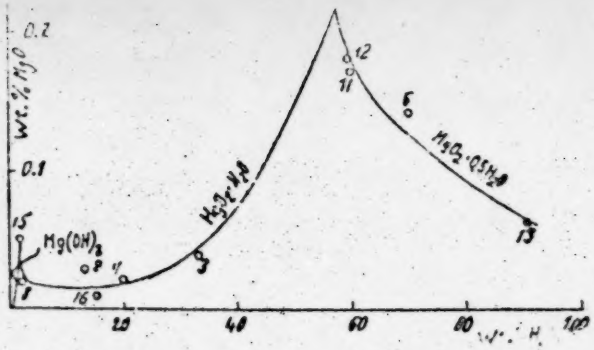


Fig. 3. 0° isotherm of the system $Mg(OH)_2-H_2O_2-H_2O$ in triangular coordinates.

Special interest attaches to the solubility isotherm (Fig. 3), plotted from data for colorimetric determination of magnesium in the liquid phase. The transition points of $Mg(OH)_2 + MgO_2 \cdot H_2O$ and $MgO_2 \cdot H_2O + MgO_2 \cdot 0.5H_2O$ correspond to conspicuous maxima which indicate the possibility of complex formation and point to definite limits to the existence of the corresponding solid phases. In comparison with water, the solubility of $Mg(OH)_2$ in which is 0.0002 wt.% in H_2O_2 solutions the solubility increases 10 times (point 8) and even 50-75 times (points 2 and 12).

20° solubility isotherm of the system $MgOH_2-H_2O_2-H_2O$. Data for the +20° isotherm of this system are set forth in Table 2 and plotted on the phase diagram (Fig. 4. As we see from Fig. 4, at 20° the solubility isotherm of the system $Mg(OH)_2-H_2O_2-H_2O$ is characterized by the presence of three solid phases: $Mg(OH)_2$ in the H_2O_2 concentration range of 0 to 2%, $MgO_2 \cdot 0.5H_2O$ in the H_2O_2 concentration range of 2 to 30%, and anhydrous magnesium peroxide in the H_2O_2 concentration range of 30 to 92%. Above this concentration equilibrium is not attained due to progressive decomposition of H_2O_2.

TABLE 2

Point Number	Liquid phase wt.% $0.5O_2$	Residue wt.% $0.5O_2$	Residue wt.% MgO	Solid Phase
12	0.55	0.55	3.20	$Mg(OH)_2$
10	0.80	12.90	32.10	$MgO_2 \cdot 0.5H_2O$
9	1.20	13.10	31.00	ditto
8	2.41	14.10	30.70	ditto
7	3.27	14.10	28.20	ditto
6	4.07	14.90	29.30	ditto
5	8.37	16.04	28.48	ditto
1	10.30	17.40	28.94	ditto
2	13.84	20.73	29.16	MgO_2
11	22.30	25.03	32.34	ditto
3	29.14	28.61	27.40	ditto
4	40.43	33.73	23.81	

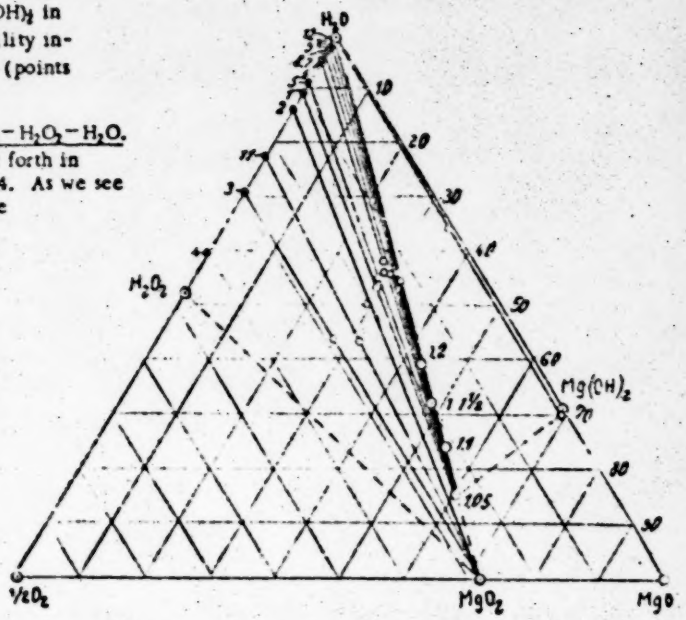


Fig. 4. 20° isotherm of the system $Mg(OH)_2-H_2O_2-H_2O$

SUMMARY

Investigation of the ternary system $Mg(OH)_2-H_2O_2-H_2O$ at 0° and at +20° by the solubility method over a wide range of concentrations of H_2O_2 established the possibility of existence of three individual peroxy compounds of magnesium with the compositions: MgO_2; $MgO_2 \cdot 0.5H_2O$ and $MgO_2 \cdot H_2O$.

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REACTION OF VITREOUS SILICATES AND SODIUM ALUMINOSILICATES WITH AQUEOUS SOLUTIONS

COMMUNICATION 4. REACTION OF VITREOUS SODIUM ALUMINOSILICATES WITH SOLUTIONS OF ACIDS

S. K. Dubrovo

In vitreous sodium aluminosilicates the aluminum is structurally analogous to silicon, as was established on the basis of an investigation of some physical properties of such glasses [1]. Nevertheless, on comparing the behavior in acid solutions of sodium silicates and the corresponding aluminosilicates, characteristic features of the presence of the aluminum ion in the glass are manifested. Evidently Sobolev's observation (to the effect that aluminosilicates, regardless of the isostructural position of the silicon and aluminum, must be regarded as double salts from the chemical standpoint) is valid [2].

In our preceding paper, on the basis of experimental data, a mechanism was advanced for the decomposition of sodium aluminosilicates by solutions of acids which involved as an initial stage a process of exchange of ions of sodium and aluminum by the hydrogen ions of the solution [3]. We should then expect the rate of decomposition of sodium aluminosilicates to be governed mainly, on the one hand, by the hydrogen ion concentration of the solution and, on the other hand, by the nature and state of the resultant products of decomposition both in solution and on the surface of the glass. The essential factor is evidently the degree of electrolytic dissociation of the salts formed in solution. From this standpoint it appeared to be a matter of extreme interest to study the interaction of aluminosilicates with solutions of various acids.

In the present paper results are submitted of a study of the decomposition of sodium aluminosilicates by solutions of sulfuric and nitric acids and also by hydrochloric acid of various concentrations.

EXPERIMENTAL

We studied the interaction of a series of vitreous sodium aluminosilicates with 0.1 N solutions of sulfuric and nitric acids, and also with 0.01 N and 1 N hydrochloric acid at 40°. The investigated aluminosilicates belonged to the sodium disilicate series with admixtures of 0.15; 0.25; 0.30; 0.40; 0.50 and 1 mole Al_2O_3. Melting of the glasses and preparation of samples were undertaken as in the previous investigations [4]. The decomposability of the aluminosilicates was determined from the amount of all the components passing from the glass into solution after a specified interval of time. The experimental procedure was the same as that previously employed by us [3]. For characterization of the process of interaction of sodium aluminosilicates with acid solutions, we used the magnitudes of n_{Na_2O}, $n_{Al_2O_3}$, n_{SiO_2}, β and α, the values of which were detailed in the preceding paper [3].

Interaction of sodium aluminosilicates with solutions of hydrochloric acid

With the objective of studying the influence of the hydrogen ion concentration of the solution on the course of decomposition of sodium aluminosilicates, an examination was made of the action of 0.01, 0.1 and 1 N hydrochloric acid solutions. These results are set forth in Tables 1 and 2. Data for the interaction of sodium aluminosilicates with 0.1 N hydrochloric acid solution were set forth in the preceding paper [3]. As we see from the data of Table 1, which show the decomposability of aluminosilicates in 0.01 N hydrochloric acid solution, admixtures with the sodium disilicate of 0.15 and 0.3 mole Al_2O_3 sharply reduce the amounts of Na_2O passing into solution from the glass in comparison with what happens in the case of the disilicate. This represents the lowest degree of decomposition. However, the degree of decomposition of the residual aluminosilicate layer increases with increasing Al_2O_3 content of the glasses, as reflected in an increase in the values of β and α. But whereas for the glass with admixture of 0.15 mole Al_2O_3 the values of β and α are extremely small and equal to one another, for the glass containing 0.3 mole Al_2O_3 there is substantially complete washing out of the aluminum ions from the decomposed layer. The amount of SiO_2 passing into solution, however, remains relatively very small (6-8%).

When the Al_2O_3 admixture to the sodium disilicate is increased to 0.4 mole, this glass suffers intensive decomposition: the quantities of all components passing into solution increase sharply, the amount of silica transferred being approximately 40% of its content in the residual layer ($\alpha = 0.4$). After treatment of the samples of glass of the composition $Na_2O \cdot 0.4Al_2O_3 \cdot 2SiO_2$ with 0.01 N hydrochloric acid solution and drying at 40°,

TABLE 1

Interaction of sodium aluminosilicates with 0.01 N hydrochloric acid solution at 40°

Molar ratio			$\frac{\text{moles}}{\text{cm}^2} 10^{-6}$	Duration in hours				
Na_2O	Al_2O_3	SiO_2		1	2	4	6	8
			β					
			α					
1	0.15	2	n_{Na_2O}	1.8	2.7	4.0	4.9	5.5
			$n_{Al_2O_3}$	–	–	–	–	0.004
			n_{SiO_2}	–	–	–	–	0.03
			β	–	–	–	–	0.004
			α	–	–	–	–	0.003
1	0.30	2	n_{Na_2O}	1.9	2.1	2.2	2.4	2.3
			$n_{Al_2O_3}$	0.7	0.8	0.8	0.7	0.7
			n_{SiO_2}	0.3	0.3	0.3	0.3	0.4
			β	1.2	1.2	1.2	0.97	1.0
			α	0.08	0.07	0.07	0.06	0.08
1	0.40	2	n_{Na_2O}	7.9	15.0	24.0	25.0	28.0
			$n_{Al_2O_3}$	3.1	6.0	8.3	8.9	9.3
			n_{SiO_2}	7.0	13.0	19.0	20	20
			β	0.98	0.97	0.85	0.88	0.85
			α	0.44	0.43	0.40	0.40	0.36
1	0.5	2	n_{Na_2O}	3.0	7.2	16.0	21	22
			$n_{Al_2O_3}$	1.5	3.2	6.7	8.9	9.3
			n_{SiO_2}	6.2	13.6	29.0	38.0	41.0
			β	1	0.90	0.85	0.85	0.85
			α	1	0.94	0.90	0.93	0.93
1	0	2	n_{Na_2O}	–	–	68	88	104
			n_{SiO_2}	–	–	0.4	1.1	2.0
			α	–	–	0.003	0.006	0.010

on their surface was observed a crumbly, friable layer. Chemical analysis of this residual layer revealed a content of approx. 96% SiO_2.

Subsequent addition of Al_2O_3 up to 0.5 mole leads to a certain drop in the amount of Na_2O passing into solution and consequently to a fall in the depth of the decomposed layer of glass in comparison with the glass of the composition $Na_2O \cdot 0.4Al_2O_3 \cdot 2SiO_2$. On the other hand, the relative amount of SiO_2 passing into solution from the residual layer increases, the value of α rises to 0.93; that of β to a little less. Possibly this is bound up with reverse adsorption by the surface of the glass of the aluminum ions passing into solution. Consequently the residual aluminosilicate layer is almost completely decomposed.

The data of Table 2 characterize the decomposability of sodium aluminosilicates in 1 N hydrochloric acid solution. They show that the first Al_2O_3 additions of 0.15 and 0.25 mole to the disilicate sharply reduce the quantity of Na_2O passing into solution. Simultaneously, starting from the composition $Na_2O \cdot 0.25Al_2O_3 \cdot 2SiO_2$, the decomposition of the aluminosilicate skeleton is intensified in the direction of preferential washing-out of aluminum ions. Unlike

TABLE 2

Interaction of sodium aluminosilicates with 1 N hydrochloric acid solution at 40°

Molar ratio			moles $\frac{}{cm^2}\ 10^{-6}$	Duration in hours				
Na_2O	Al_2O_3	SiO_2		1	2	4	6	8
1	0.15	2	n_{Na_2O}	2.1	2.8	3.8	3.9	4.9
			$n_{Al_2O_3}$	–	–	–	–	–
			n_{SiO_2}	–	–	–	–	–
			β	–	–	–	–	–
			α	–	–	–	–	–
1	0.25	2	n_{Na_2O}	1.2	1.4	1.9	2.3	2.4
			$n_{Al_2O_3}$	0.21	0.21	0.19	0.19	0.19
			n_{SiO_2}	0.03	0.07	0.14	0.14	0.21
			β	0.07	0.60	0.40	0.33	0.32
			α	0.012	0.025	0.036	0.030	0.043
1	0.30	2	n_{Na_2O}	11	31	68	92	133
			$n_{Al_2O_3}$	3.7	7.5	15.0	24.0	31.0
			n_{SiO_2}	1.4	2.0	3.6	5.0	7.9
			β	1.1	0.80	0.75	0.85	0.77
			α	0.064	0.032	0.029	0.032	0.030
1	0.40	2	n_{Na_2O}	69.2	141	300	442	603
			$n_{Al_2O_3}$	29.2	57.2	115	176	240
			n_{SiO_2}	59	74-118	125-183	164-247	292
			β	1.05	1.01	0.96	1.0	1.0
			α	0.42	0.37-0.42	0.20-0.30	0.20-0.28	0.24
1	0.50	2	n_{Na_2O}	69	148	336	573	830
			$n_{Al_2O_3}$	37	80	163	255	350
			n_{SiO_2}	136	300	612	962	1232
			β	1.01	1.08	0.91	0.89	0.84
			α	0.99	1.01	0.91	0.84	0.70
1	1	2	n_{Na_2O}	–	67	160	219	307
			$n_{Al_2O_3}$	–	70	153	208	298
			n_{SiO_2}	–	138	273	450	592
			β	–	1.04	0.95	0.95	0.97
			α	–	1.03	0.89	1.02	0.96
1	0	2	n_{Na_2O}	25.3	41	64	88	105
			n_{SiO_2}	0	0	0	0	0

the action of weaker solutions of hydrochloric acid (0.01 and 0.1 N) a sharp rise in the amount of Na_2O going into solution commences even with a composition containing 0.3 mole Al_2O_3.

TABLE 3

Reaction of sodium aluminates with 0.1 N sulfuric and hydrochloric acid solutions at 40°

Molar ratio			moles / cm² 10⁻⁶	Duration in hours					Acid
Na_2O	Al_2O_3	SiO_2		1	2	4	6	8	
1	0.15	2	n_{Na_2O}	2.6	3.8	4.3	5.1	6.8	
			$n_{Al_2O_3}$	—	—	—	0	0	
			n_{SiO_2}	—	—	—	0	0	
			β	—	—	—	0	0	0.1 N
			α	—	—	—	0	0	H_2SO_4
1	0.15	2	n_{Na_2O}	1.7	2.4	3.7	4.3	4.7	
			$n_{Al_2O_3}$	—	—	—	0.014	0.016	
			n_{SiO_2}	—	—	—	0.010	0.014	0.1 N
			β	—	—	—	0.02	0.02	HNO_3
			α	—	—	—	0.001	0.002	
1	0.30	2	n_{Na_2O}	4.4	8.4	12	14	14	
			$n_{Al_2O_3}$	1.5	2.3	3.1	3.6	3.7	
			n_{SiO_2}	0.5	0.8	1.2	1.4	1.6	0.1 N
			β	1.1	0.90	0.83	0.86	0.91	H_2SO_4
			α	0.056	0.047	0.048	0.050	0.051	
1	0.40	2	n_{Na_2O}	29	58	108	145	174	
			$n_{Al_2O_3}$	12	24	43	55	68	
			n_{SiO_2}	29	59	121	140	176	0.1 N
			β	1.03	1.03	1.0	0.95	0.99	H_2SO_4
			α	0.50	0.51	0.54	0.48	0.51	
1	0.40	2	n_{Na_2O}	13	26	55	87	115	
			$n_{Al_2O_3}$	5.0	9.6	22	32	44	
			n_{SiO_2}	20	32	57	83	95	0.1 N
			β	0.96	0.92	1.0	0.92	0.97	HNO_3
			α	0.77	0.61	0.52	0.48	0.40	
1	0.50	2	n_{Na_2O}	36	81	148	175	201	
			$n_{Al_2O_3}$	18	37	69	82	87	
			n_{SiO_2}	76	152	275	335	369	0.1 N
			β	1	0.91	0.95	0.93	0.87	H_2SO_4
			α	0.05	0.94	0.94	0.96	0.92	

TABLE 3 (cont.)

Molar ratio			moles / cm² · 10⁻⁶	Duration in hours					Acid
Na_2O	Al_2O_3	SiO_2		1	2	4	6	8	
1	0,50	2	n_{Na_2O}	9,8	22	46	75	92	
			$n_{Al_2O_3}$	5,1	10	23	33	45	
			n_{SiO_2}	21	43	86	135	196	0,1 N
			β	1,04	0,93	1,0	0,90	0,98	HNO_3
			α	1,06	0,97	0,96	0,90	1,02	
1	1	2	n_{Na_2O}	16	37	76	120	156	
			$n_{Al_2O_3}$	14	25	66	106	144	
			n_{SiO_2}	29	65	148	217	278	0,1 N
			β	0,83	0,70	0,86	0,81	0,84	H_2SO_4
			α	0,90	0,87	0,98	0,80	0,91	
1	0	2	n_{Na_2O}	26	52	74	94	119	
			n_{SiO_2}	0,05	0,04	0,14	0,23	0,60	0,1 N
			α	0,001	0,0004	0,0010	0,0010	0,003	H_2SO_4

Further additions of 0,4 and 0,5 mole Al_2O_3 intensify the decomposability of the glasses, the absolute amounts of all components passing into solution being increased. During this process the Al_2O_3 is completely washed out from the residual layer of the glass of composition $Na_2O \cdot 0,4Al_2O_3 \cdot 2SiO_2$. The quantities of SiO_2 passing into solution, however, amounted at the start to approximately 40% of its content in the residual layer (as in the action of less concentrated acids), after which these amounts progressively decreased. Addition of 0,5 mole Al_2O_3 to sodium disilicate leads to a further increase in the amounts of all components passing into solution, while the ratio of Al_2O_3 and SiO_2 in the solution is substantially equal to their original ratio in the starting glass. A process of dissolution, as it were, of the glass of composition $Na_2O \cdot 0,5Al_2O_3 \cdot 2SiO_2$ in 1 N hydrochloric acid takes place, as was the case in the action of an 0,1 N solution of the same acid. With passage of time, however, as we see from Table 2, α and β decrease. This must evidently be the result of a secondary process of partial coagulation at the surface of the glass, of the silica which had accumulated in the solution and whose concentration in the experimental conditions reached 0,01 g/ml. The coagulating silica could adsorb aluminum ions. The later increase to 1 mole of the Al_2O_3 content of the sodium aluminosilicate results in a drop in the absolute amounts of components going into solution, although the character of the decomposition remains essentially the same as when 0,5 mole Al_2O_3 had been added.

Interaction of sodium aluminosilicates with solutions of sulfuric and nitric acids

In Table 3 are set forth the results of a determination of the decomposability of sodium aluminosilicates in 0,1 N solutions of sulfuric and nitric acids. As is evident from the data for all the three aluminosilicates investigated, the amounts of components going into solution on interaction with 0,1 N solution of nitric acid are approximately the same as on interaction with hydrochloric acid of the same concentration. The action of 0,1 N sulfuric acid solution on all the investigated aluminosilicates is considerably more intensive than that of hydrochloric and nitric acids, although the character of the decomposition remains identical over the range of compositions studied. The decomposition of the aluminosilicate skeleton likewise proceeds in the direction of preferential removal of aluminum ions. The relative amounts of SiO_2 passing into solution thus increase with increasing content of Al_2O_3 in the composition of the investigated glasses. For the composition $Na_2O \cdot 0,5Al_2O_3 \cdot 2SiO_2$ passage into solution of the Al_2O_3 and SiO_2 takes place in the same ratios as those which were present in the original glass, and this occurred in the case of both hydrochloric and nitric acid. A fall in the degree of decomposition of sodium aluminosilicates in 0,1 N sulfuric acid solution is observed in passing from a composition containing 0,5 mole Al_2O_3 to a composition to which 1 mole Al_2O_3 was added. In contrast to what happens in treatment with 0,1 N

TABLE 4

Amount of molecularly dispersed silica in the samples in %

Molar ratio			Acid used	Duration of action (hours)	SiO_2 conc. ($g/ml \cdot 10^{-4}$)	Amount of molecularly dispersed silica in % of its total content in the solution
Na_2O	Al_2O_3	SiO_2				
1	0.3	2	1 N HCl	6	0.62	98
1	0.3	2	1 N HCl	8	0.58	95
1	0.4	2	0.01 N HCl	8	1.2	94
1	0.5	2	ditto	6	2.4	72
1	0.5	2	ditto	8	2.2	76
1	0	1.7	0.1 N HCl	3	2.6	52
1	0	1.7	ditto	4	6.3	47
1	0.5	2	ditto	6	8.1	66
1	0.5	2	ditto	8	11.4	66
1	0.4	2	1 N HCl	6	19	53
1	0.5	2	0.1 N H_2SO_4	6	20	78
1	0.5	2	0.1 N H_2SO_4	8	22.0	73
1	0.4	2	1 N HCl	8	25.5	35

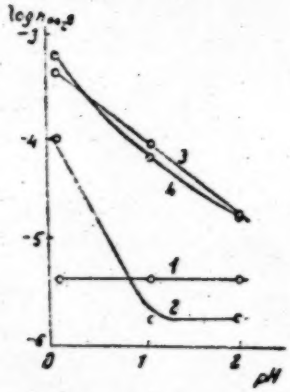

Fig. 1. Dependence of leaching out of Na_2O on the pH of the reacting solution of hydrochloric acid. 1) glass with the composition $Na_2O \cdot 0.15Al_2O_3 \cdot 2SiO_2$; 2) glass with composition $Na_2O \cdot 0.30Al_2O_3 \cdot 2SiO_2$; 3) glass with composition $Na_2O \cdot 0.40Al_2O_3 \cdot 2SiO_2$; 4) glass with composition $Na_2O \cdot 0.50Al_2O_3 \cdot 2SiO_2$.

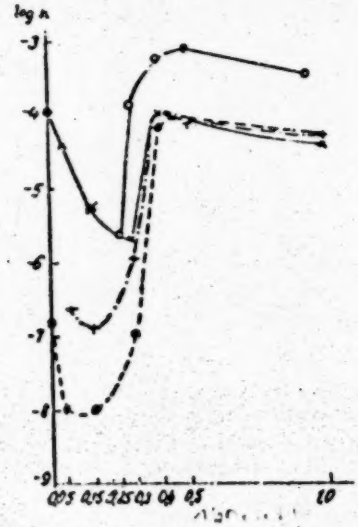

Fig. 2. Dependence of decomposability of sodium aluminosilicates in acids of various concentrations on the Al_2O_3 content: o) $\log n_{Na_2O}$ 1N HCl; ,) $\log n_{Na_2O}$, 0.1 N HCl; +) $-\log \frac{n_{Al_2O_3}}{k}$, 0.1 N HCl, o) $-\log \frac{n_{SiO_2}}{2}$, 0.1 N HCl

hydrochloric acid, an 0.1 N sulfuric acid solution increases the amount of Na_2O going into solution on passing from a composition with addition of 0.15 mole Al_2O_3 to one with 0.30 mole Al_2O_3. In this respect 0.1 N sulfuric acid occupies a position intermediate between 0.1 and 1 N hydrochloric acid solutions.

State of the silica passing into solution

In the colorimetric determination of the silica passing into solution from the investigated glasses on the basis of the yellow silicomolybdate complex, we applied in all cases a preliminary "resuscitation" of the SiO_2 by boiling with 1 N NaOH solution, since silicic acid in acidic solutions has a tendency to polymerize. As we know, however, polymerized silicic acid to a considerable extent is not determined colorimetrically [5]. In a parallel series of experiments we also carried out determinations of SiO_2 without preliminary resuscitation. This gave us the possibility of establishing how much silica is present at a given instant in the molecular state in the sample; this knowledge facilitated clarification of the character of the interaction of sodium aluminosilicates with solutions of acids.

In Table 4 are set forth the data for determination of the content of molecularly dispersed silica in the individual samples. We see from these data that the quantities of molecularly dispersed silica in the solution vary in our experiments from 35 to 98% of its total content. The very fact of the presence in the solution of colorimetrically determinable silica is proof that the silica passing into solution is close to the molecularly dispersed state.

Subsequently the polymerization of the silicic acid proceeds with varying velocity in dependence on the concentration of silicic acid in solution, on the character and concentration of the acid acting on the glass, and on the duration of the reaction.

Interest attaches to the fact that when using 0.1 N sulfuric acid the content of molecularly dispersed silica in the solution is higher than when using 0.1 N hydrochloric acid, notwithstanding that in the first case the total SiO_2 concentration is twice as high (see Table 4). This may be explained by the lower activity of sulfuric acid, due to which the silicic acid polymerizes more slowly.

Evaluation of Results

The hydrogen ion concentration of the reacting medium is one of the fundamental factors influencing the rate of decomposition of sodium aluminosilicates. A series of other factors which come into play during the process may, however, mask the influence of the change of hydrogen ion concentration. Such factors are a residual layer on the surface of the glasses which regulates the diffusion of ions, the degree of dissociation of the salts formed in solution, etc.

In Figure 1 is plotted the logarithmic dependence on the pH of the hydrochloric acid solutions of the amounts of Na_2O leached out of the glasses. This diagram shows that increase of hydrogen ion concentration is accompanied by intensified decomposition of the aluminosilicate glasses containing relatively large amounts of Al_2O_3, the skeleton of these glasses, due to depolymerization of the contained silica, being unstable toward acidic solutions. And on the surface of such aluminosilicates, as we have seen, either no residual surface layer is formed or this layer is a crumbly and weakly attached hydrated silica. In such cases the decomposability will be mainly governed by the hydrogen ion concentration when using one and the same acid in various concentrations.

In the case of aluminosilicates containing an addition of up to 0.3 mole Al_2O_3 to the disilicate, a change of hydrogen ion concentration in the acidic region has substantially no effect on their speed of decomposition. The same observation is made in the case of sodium silicates [4]. This phenomenon may be explained in the following way (by analogy with the case of silicates [6]). Due to the formation on the surface of these aluminosilicates of a protective residual aluminosilicate film on reaction with solutions of hydrochloric acid, a masking factor comes into play in the form of diffusion of the exchanging ions through this film. The velocity of diffusion of the sodium ions is governed, however, by their concentration difference in this film. When using acids at the limits of the above-indicated values of pH, the concentration of sodium ions in the residual film at the boundary with the solution is close to zero. Hence the difference of concentrations of the sodium ions in the surface film is at a maximum and is substantially independent of the hydrogen ion concentration.

In Figure 2 is plotted the dependence of the logarithm of the amounts of glass components passing into solution on the additions of Al_2O_3 to the sodium disilicate compound when these glasses are treated with 0.1 and 1N solutions of hydrochloric acid. We see that the increase in concentration of hydrochloric acid over the indicated range shifts the stability maximum into the region of aluminosilicates with a lower Al_2O_3 content. This reflects the absence of correlation between decomposability and the position of the singular points on the investigated portion of the phase diagram of the system $Na_2O-Al_2O_3-SiO_2$.

The curves of Figure 2 illustrate the character of the decomposition of vitreous sodium aluminosilicates. For glasses with addition of up to 0.15 mole Al_2O_3 to the disilicate, the decomposition is mainly characterized by a process of leaching-out of Na_2O. With increasing content of Al_2O_3 there is a fall in the stability of the aluminosilicate skeleton from which the aluminum ions are washed out in the first instance. The Na_2O and Al_2O_3 leaching curves substantially coincide. Passage into solution of SiO_2 from aluminosilicate glasses lags behind that of other components up to a composition with an Al_2O_3 content of 0.5 mole Al_2O_3.

Silicic acid is capable of passing into solution, when the investigated sodium aluminosilicates are treated with acids, either in the ionic form or in a state close to molecular dispersion. Evidence of this, as indicated above, is the presence in the acid extracts of silicic acid which is directly determinable by a colorimetric method. Passage into solution of silicic acid in the form of ions or in a highly dispersed state has also been observed by Kruger [7] who studied the action of acids on natural lecite by the method of electrodialysis.

A comparison of the decomposability of the investigated aluminosilicates in various acids reveals that 0.1 N sulfuric acid acts more intensively than hydrochloric or nitric acid of the same concentration. We may suggest that this is due to the differing degrees of dissociation of the respective salts which are formed in solution by exchange of the sodium and aluminum ions of the glass by hydrogen ions of the solution.

Acids like hydrochloric and nitric possess a higher mean coefficient of activity than sulfuric acid of the same concentration. In the light of what has been suggested above about the influence of the hydrogen ion concentrations, we ought to expect a higher velocity of decomposition of aluminosilicates in solutions of the former acids. As we know, however, in passing from singly charged to multiply charged ions there is a sharp fall in the degree of dissociation of the resultant electrolytes [8]. Consequently the sodium sulfate and, in particular, the aluminum sulfate formed in the solution will be very much less dissociated than the corresponding chlorides and nitrates. And this difference will be greater than the difference in the degree of electrolytic dissociation of hydrochloric and sulfuric acids. The concentration of sodium and aluminum ions in the solution decreases sharply in the case of reaction with sulfuric acid in comparison with reaction with hydrochloric and nitric acids, due to which the removal of sodium and aluminum ions from the glass is accelerated.

Consequently, as follows from the considerations put forward above, a number of factors govern the rate of decomposition of vitreous sodium aluminosilicates in solutions of acids. The most important of these are the hydrogen ion concentration of the reacting solution, the state of the residual aluminosilicate surface film, and the degree of dissociation of the electrolytes which are formed in solution.

SUMMARY

1. A study was made of the reaction with solutions of hydrochloric, nitric and sulfuric acids of vitreous sodium aluminosilicates composed of disilicate with additions of 0.15 to 1 mole Al_2O_3.

2. Increasing hydrogen ion concentration when using one and the same acid is accompanied by increasing decomposability of those aluminosilicate glasses whose skeleton, due to depolymerization of their silica content, is unstable toward solutions of acids.

3. Vitreous sodium aluminosilicates are decomposed in 0.1 N sulfuric acid solution more rapidly than in hydrochloric and nitric acids of the same concentration. This phenomenon can be explained by the lower degree of electrolytic dissociation in comparison with the corresponding chlorides and nitrates formed in a solution of sodium and aluminum sulfates.

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REACTION OF VITREOUS SODIUM SILICATES AND ALUMINOSILICATES WITH AQUEOUS SOLUTIONS

COMMUNICATION 5. REACTION OF VITREOUS SODIUM ALUMINOSILICATES WITH WATER

Yu. A. Shmidt

In previous communications we described the reaction of vitreous sodium silicates with aqueous solutions [1,2], and also the reaction of vitreous sodium aluminosilicates with solutions of acids [3,4]. The present paper deals with the reaction of vitreous sodium aluminosilicates with water.

The literature on this topic is very scanty. Dimbleby and Turner [5], studied six sodium aluminosilicate glasses which were prepared by successive substitution in a starting glass, composition $Na_2O \cdot 3SiO_2$, of up to 0.3 mole Na_2O by alumina (in 0.05 mole steps). They determined the loss in weight of powders of the glass after boiling in water. In a study by Enss [6] the starting substance was a glass composed of Na_2O 18% and SiO_2 82%, in which part of the silica was replaced by alumina. After heating the powdered glass in water at 100°, the Na_2O, Al_2O_3 and SiO_2 contents of the solution were determined. Our recalculation of Enss' results shows that the leached surface film of the glass is slightly enriched with alumina by comparison with the original glass. Studies [5] and [6] also showed that the chemical stability of the glasses rises appreciably with increasing content of alumina and that a relatively greater effect is exerted by the first, small, additions. In a study of the decomposition of feldspars by aqueous solutions, Correns [7] showed that in acidic and alkaline media the leached film contains less alumina and in a neutral medium it contains more alumina than the original mineral. The author correlates this behavior with the amphoteric character of alumina, which in the neutral region possesses minimum solubility.

EXPERIMENTAL

The reaction with water was studied of twelve vitreous sodium aluminosilicates prepared by adding various amounts of alumina to the previously studied sodium silicates (see Table 1). The position on the phase diagram of the silicates and aluminosilicates investigated in the present research and in the above-noted papers [5,6] are shown in Figure 1. The chemical analysis of the investigated glasses of the sodium disilicate series has been previously reported [3].

TABLE 1

Composition of the sodium aluminosilicates studied

Starting silicate	Aluminosilicates				
Molar ratio of $Na_2O : SiO_2$	Molar ratio of $Na_2O : Al_2O_3 : SiO_2$				
1:1.4	1:0.05:1.4	1:0.15:1.4	1:0.3:1.4	—	—
1:1.7	1:0.05:1.7	1:0.15:1.7	1:0.3:1.7	—	—
1:2	1:0.05:2	1:0.15:2	1:0.3:2	1:0.5:2	1:1:2
1:3	1:0.05:3	—	—	—	—

Experiments were carried out at 40° by the previously described procedure [1,3], i.e., by determination of the quantity of components passing into solution after a specified period of reaction of the sample with water. In the case of the aluminosilicate with the composition $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ the amounts of components passing into solution were so small that we decided to resort to the powder method. We used a glass powder with a particle size of 110-140 μ, thoroughly washed free from dust with ethanol and dried at 110°. The calculated surface area of the weighed sample (0.8 g) used was approx. 160 cm^2. As previously, we characterized the process of reaction on the basis of the magnitudes of n_{Na_2O}, $n_{Al_2O_3}$, and n_{SiO_2} (representing the amount of the respective oxides passing from the glass into solution from 1 cm^2 of glass surface), and also with reference to the magnitudes of α and β (representing the proportions of Al_2O_3 and SiO_2 passing into solution from the surface film of the glass brought into reaction with the solution).

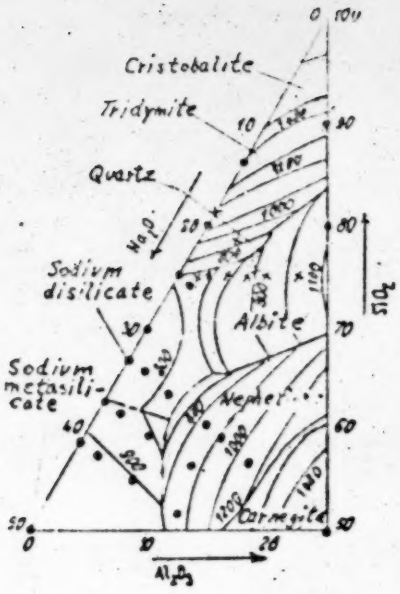

Fig. 1. Position of the investigated compositions on the $Na_2O-Al_2O_3-SiO_2$ phase diagram
- compositions studied in the present investigation; X - studied by Dimbleby and Turner; + - studied by Enss.

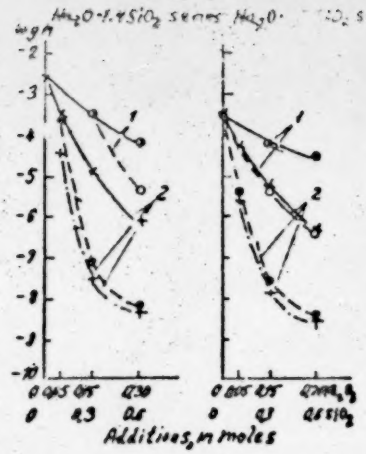

Fig. 2. Comparison of amounts of components passing into solution after 6 hours' reaction with water of vitreous sodium silicates and aluminosilicates (1 - silicates; 2 - aluminosilicates): $\log n_{Na_2O}$; $\log \frac{n_{Al_2O_3}}{k}$; $\log \frac{n_{SiO_2}}{m}$

(k and m are the Al_2O_3 and SiO_2 contents of the glass expressed in the form $Na_2O \cdot kAl_2O_3 \cdot mSiO_2$.)

In view of the fact that the regularities observed in the investigated series of aluminosilicates were analogous, we shall in the future concentrate for the most part on the sodium disilicate series which we studied up to addition of one mole alumina. Results of investigation of reaction with water of some glasses of this series over various intervals are set forth in Table 2. In Figures 2 and 3 are compared the amounts of components passing into solution after six hours' reaction with water of the vitreous sodium silicates and aluminosilicates investigated by us. On the basis of these data and of literature data [8,9] we suggest that aluminum enters into the structure of the studied glasses in fourfold coordination as an analog of silicon, and that consequently 0.5 mole alumina is approximately equivalent to one mole of silica in the structure of the glass.

From the data obtained we see that addition of alumina to sodium disilicate is accompanied by a continuous drop in the amounts of Na_2O passing into solution, this drop being relatively more pronounced with small additions. Up to additions of 0.15 mole Al_2O_3 the values of $n_{Al_2O_3}$ and n_{SiO_2} are reduced very much more quickly than the magnitude of n_{Na_2O}. With further increase of the additions of alumina (0.3 and 0.5 mole) the fall in values of $n_{Al_2O_3}$ and n_{SiO_2} becomes less marked, and later it ceases entirely. On transition to the composition $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ these values rise appreciably. A consequence of the described change of $n_{Al_2O_3}$ and n_{SiO_2} is that the magnitudes of α and β, which at first (up to addition of 0.15 mole Al_2O_3) fell off, subsequently started to rise again and for the composition $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ they reached fairly high values ($\alpha = 0.42$, $\beta = 0.17$).

Comparison of the data obtained for aluminosilicates with an identical (in moles) addition of alumina shows that with increase of their silica content the amount of components passing into solution continuously decreases, in analogy with what took place in the sodium disilicate series. It should also be noted that the magnitude of β in all cases is lower than that of α, thus pointing to enrichment of the surface film with alumina.

Evaluation of results

As we have already reported [3,4], with increasing addition of alumina to sodium silicates there is an increase in the total number of Si - O - Al bonds. In other words the degree of polymerization of the aluminosilicate skeleton of the glass increases. The number of Si - O - Si bonds, however, i.e., the degree of polymerization of the silica portion of the skeleton, decreases during the process. For this reason, the influence of alumina on the reaction of glasses with aqueous solutions has a dual character.

TABLE 2

Reaction of some aluminosilicates of the disilicate series with water

Composition of glass	Characteristics	Duration in hours				
		1	2	4	6	8
$Na_2O \cdot 2SiO_2$	$n_{Na_2O} \cdot 10^{-6}$	18	30	47	62	76
	$n_{SiO_2} \cdot 10^{-6}$	3.2	4.2	5.8	9.3	13
$Na_2O \cdot 0.05Al_2O_3 \cdot 2SiO_2$	$n_{Na_2O} \cdot 10^{-6}$	8.0	11	17	22	25
	$n_{Al_2O_3} \cdot 10^{-6}$	0.003	0.005	0.012	0.020	0.024
	$n_{SiO_2} \cdot 10^{-6}$	0.022	0.34	0.64	1.2	1.4
	α	0.014	0.015	0.019	0.027	0.028
	β	0.008	0.009	0.014	0.018	0.019
$Na_2O \cdot 0.15Al_2O_3 \cdot 2SiO_2$	$n_{Na_2O} \cdot 10^{-6}$	1.5	2.0	2.7	3.3	3.8
	$n_{Al_2O_3} \cdot 10^{-6}$	—	—	—	0.001	—
	$n_{SiO_2} \cdot 10^{-6}$	—	—	—	0.022	—
	α	—	—	—	0.003	—
	β	—	—	—	0.002	—
$Na_2O \cdot 0.3Al_2O_3 \cdot 2SiO_2$	$n_{Na_2O} \cdot 10^{-6}$	0.18	0.22	0.26	0.31	0.34
	$n_{Al_2O_3} \cdot 10^{-6}$	—	—	—	0.0004	—
	$n_{SiO_2} \cdot 10^{-6}$	—	—	—	0.004	—
	α	—	—	—	0.006	—
	β	—	—	—	0.004	—

On the one hand an increase in the degree of polymerization of the aluminosilicate framework of the glass strengthens all the bonds, as was the case when the silica content of vitreous sodium silicates was increased [1]. Consequently the amounts of Na_2O passing into solution (likewise the amounts of Al_2O_3 and SiO_2 when the amounts of alumina added are small) decrease sharply. The influence of the alumina is then very much greater than that of the equivalent amounts of silica. Attention must also be directed to the fact that the addition to sodium disilicate of only 0.05 mole Al_2O_3 lowers the value of n_{Na_2O} 2.8 times and that of n_{SiO_2} 7.8 times (the values are compared after 6 hours' reaction). Further increase of the content of alumina to 0.15 mole lowers these values (by comparison with disilicate) 19 and 420 times respectively. At the same time it is easy to calculate that in the case of addition of 0.05 mole Al_2O_3 only 5% of the total number of sodium ions and 10% of the SiO_4 tetrahedra are directly bound to the AlO_4 tetrahedra, while in the case of addition of 0.15 mole Al_2O_3 the amounts are respectively 15 and 60%. These data indicate that the influence of the aluminum extends not only to those sodium ions and SiO_4 tetrahedra which are directly linked to the AlO_4 tetrahedra but also to the whole structure of the glass. Slight depolymerization of the silicate portion of the framework with small additions of alumina does not occur to an appreciable extent since the AlO_4 tetrahedra are surrounded by a large number of SiO_4 tetrahedra and are thereby protected against the action of the solution.

When the alumina content in the sodium disilicate series is increased to 0.3 mole and higher the number of Si–O–Al bonds is then higher than the number of Si–O–Si bonds, the AlO_4 tetrahedra becoming more accessible to the action of the solution. Hence, as was shown in previous communications [3,4], depolymerization of the silicate portion of the framework beyond the above-indicated limit has the consequence that under the action of solutions of acids which extract aluminum ions from the residual film, this film at first becomes loose and then completely decomposes.

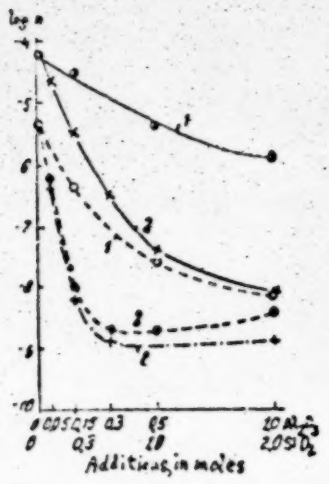

Fig. 3. Comparison of amounts of components passing into solution after 6 hours' reaction with water of vitreous sodium silicates and aluminosilicates (sodium disilicate series: 1 - silicates; 2 - aluminosilicates) — $\log n_{Na_2O}$; - - $\log \frac{Al_2O_3}{k}$; - · - · $\log \frac{n_{SiO_2}}{m}$

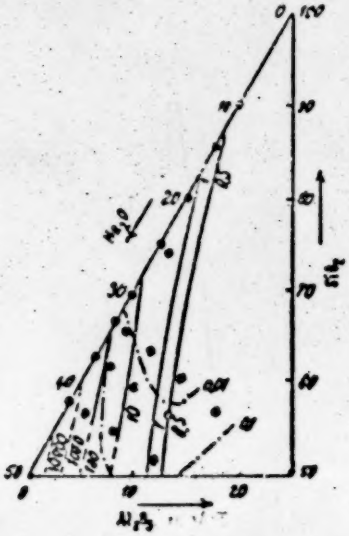

Fig. 4. Amount of Na_2O (in moles/$cm^2 \cdot 10^{-6}$) passing into solution and magnitude of a as functions of the composition of the studied glasses: ——— n_{Na_2O}; — — — a

When the glasses react with water, the passage of aluminum ions into solution is inhibited by the near insolubility of alumina in neutral and weakly alkaline solutions, due to which there is no intensive decomposition of the film. Increase, however, of the content of alumina in the sodium disilicate series to more than 0.3-0.5 mole leads nevertheless to a slight increase in the amounts of Al_2O_3 and SiO_2 passing into solution. Increase in the silica content of the composition of the vitreous sodium aluminosilicates is accompanied by an increased degree of polymerization both of the aluminosilicate framework as a whole and of the silicate portion, due to which the quantity of components passing into solution continuously diminishes.

As was pointed out above, the alumina content of the residual film is observed in all the experiments to be higher than that of the original glass. It may therefore be suggested that during the primary process of exchange of the sodium ions of the glass by hydrogen ions from the solution which leads to formation of a film, the bonds between the AlO_4 and SiO_4 tetrahedra entering into the aluminosilicate framework are not broken. Enrichment of the film itself with alumina evidently occurs as the result of reverse adsorption of those aluminum ions which had gone into solution from the portion of the film which had been completely decomposed in the course of the experiment. If we know the composition of the resultant solution, we can make a rough calculation of both the total content of aluminum in the film and of the content of aluminum entering into the aluminosilicate framework of the film and, separately, adsorbed by it. Calculations show that with increasing stability of the aluminosilicates, both the absolute and relative content of aluminum adsorbed in the film falls sharply and amounts to not more than 0.2-0.5 % of its total content. This enables us to conclude that the main influence upon the stability of the residual film is evidently exerted by the aluminum ions entering into the structure of its aluminosilicate framework. The small amount of adsorbed aluminum ions, however, which are retained in the film by relatively weak adsorption forces can hardly exert an appreciable influence on its stability. This view is also strengthened by experiments in an acid medium [3,4] with small additions of alumina which brought about strengthening of the film. In spite of the fact that in an acid medium the aluminum content of the film is reduced,

due to which its reverse adsorption is obviously insignificant, the values of n_{Na_2O} prove to be close to those obtained in experiments with water. The small difference in values of n_{Na_2O} which nevertheless arise may be accounted for by the high hydrogen ion concentration in the acidic medium [2] and not by difference in the stability of the film.

In Figure 4 lines have been plotted by interpolation which correspond to equal amounts of Na_2O passing into solution in the investigated region of compositions. On the same diagram (dot-dash curves) are shown plots corresponding to the values of $\alpha = 0.1$ and 0.01. A comparison of Figures 1 and 4 does not reveal any correspondence whatever between the amount of components passing into solution and the phase diagram of the system $Na_2O-Al_2O_3-SiO_2$.

SUMMARY

1. Increase in the alumina content of sodium aluminosilicates is accompanied by an increased degree of polymerization of the aluminosilicate framework of the glass, leading to a considerable drop in the amounts of Na_2O passing into solution as well as (in the case of small additions of alumina) of the amounts of Al_2O_3 and SiO_2 passing into solution. In this connection the influence of alumina is much stronger than that of equivalent amounts of silica.

2. When the alumina content increases beyond a certain limit, the depolymerization of the silicate portion of the framework weakens the stability of the residual film at the surface of vitreous sodium aluminosilicates.

3. An increase of the silica content continuously reduces the amounts of components passing into solution.

4. A large proportion of the aluminum ions in the residual film enters into the composition of its aluminosilicate framework and therefore has an essential influence on its strength. A small proportion of the aluminum ions is evidently retained by the film in the adsorbed state.

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ABSORPTION SPECTRA OF PYRILIUM SALTS

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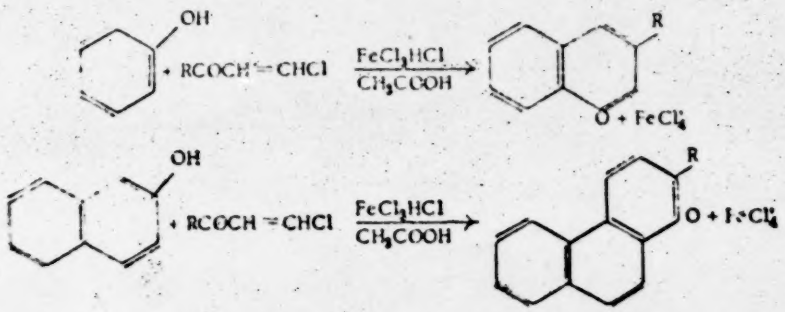
Three of us have realized a new synthesis of benzopyrilium [1], flavylium [1] and naphthopyrilium [1,2] salts. These compounds, prepared according to the scheme



in the form of oxonium salts containing the $FeCl_4$ anion, form intensely colored crystalline powders, soluble in glacial acetic acid. One of them, 7-hydroxy-4'-methoxyflavylium chloride, contains a cation which is the methyl derivative of the anthocyanidine, hesperidine, found in Gensenetia cardinalis.

The literature contains rather scanty data for the absorption spectra of pyrilium salts. Wizinger plotted the absorption spectra of various distyrylpyrilium salts [3] and of some flavylium salts [4], but he only gave the wavelengths of the absorption maxima. We took advantage of the great possibilities of the new spectrophotometer constructed by Dianov-Klokov in the laboratory of I. V. Obreimov (Institute of Organic Chemistry of the Academy of Sciences USSR) to plot the absorption spectra of the following pyrilium salts: benzopyrilium – 2-methylbenzopyrilium ferrichloride (I), 2,6-dimethylbenzopyrilium ferrichloride (II), 6-hydroxy-2-methylbenzopyrilium ferrichloride (III), and 7-hydroxy-2-methylbenzopyrilium ferrichloride (IV); flavylium – flavylium ferrichloride (V), 2-methylflavylium ferrichloride (VI), 4',6-dimethylflavylium ferrichloride (VII), 4'-bromo-6-methylflavylium ferrichloride (VIII), 6-hydroxyflavylium ferrichloride (IX), 4'-bromo-6-hydroxyflavylium ferrichloride (X), 4'-bromo-7-hydroxyflavylium ferrichloride (XII), 7-hydroxy-4'-methoxyflavylium ferrichloride (XIII); naphthopyrilium salts – 2-methylnaphthopyrilium ferrichloride (XIV), 2-propylnaphthopyrilium ferrichloride (XV), 2-isopropylnaphthopyrilium ferrichloride (XVI), 2-isobutylnaphthopyrilium ferrichloride (XVII), 2-amylnaphthopyrilium ferrichloride (XVIII), 2-phenylnaphthopyrilium ferrichloride (XIX), 2-p-tolylnaphthopyrilium ferrichloride (XX), 2-p-bromophenylnaphthopyrilium ferrichloride (XXI), 2-p-methoxyphenylnaphthopyrilium ferrichloride (XXII), and 2-methylnaphthopyrilium perchlorate (XXIII).

Spectra of pyrilium salts in acetic acid were plotted in the 587 to 334 mμ region at 10^{-4} concentration of solutions, the curves of the absorption spectra (ratio of I/I_0) obtained on the oscillograph were directly photographed onto a plate. At a later date we intend to plot the absorption curves of the enumerated compounds in the ultraviolet region.

In order to establish the effect of the contribution of the anion in the plotted spectrum, we plotted the spectrum of ferric chloride in a solution of acetic and hydrochloric acids. It was found that appreciable absorption of the $FeCl_4^-$ anion commences at a concentration of 10^{-3} and its absorption can clearly not bring about a serious change in the spectra of the salts, since we carried out the examination of the absorption spectra of the pyrilium salts at a concentration of 10^{-4}. In order to determine the influence of various anions upon the character of the absorption, we plotted the absorption spectra of 2-methylnaphthopyrilium ferrichloride and perchlorate. We see from the photographs (XXIII and XIV) that the spectrum of the salt does not substantially alter with change of anion. We may therefore assume that the absorption spectra of the investigated compounds are governed by the organic portion of the molecule.

The spectra of the investigated pyrilium salts differ profoundly in dependence on the structure; in respect of the character of the absorption spectra all the investigated substances may be arranged into three groups: benzopyrilium, flavylium, and naphthopyrilium salts.

Benzopyrilium salts

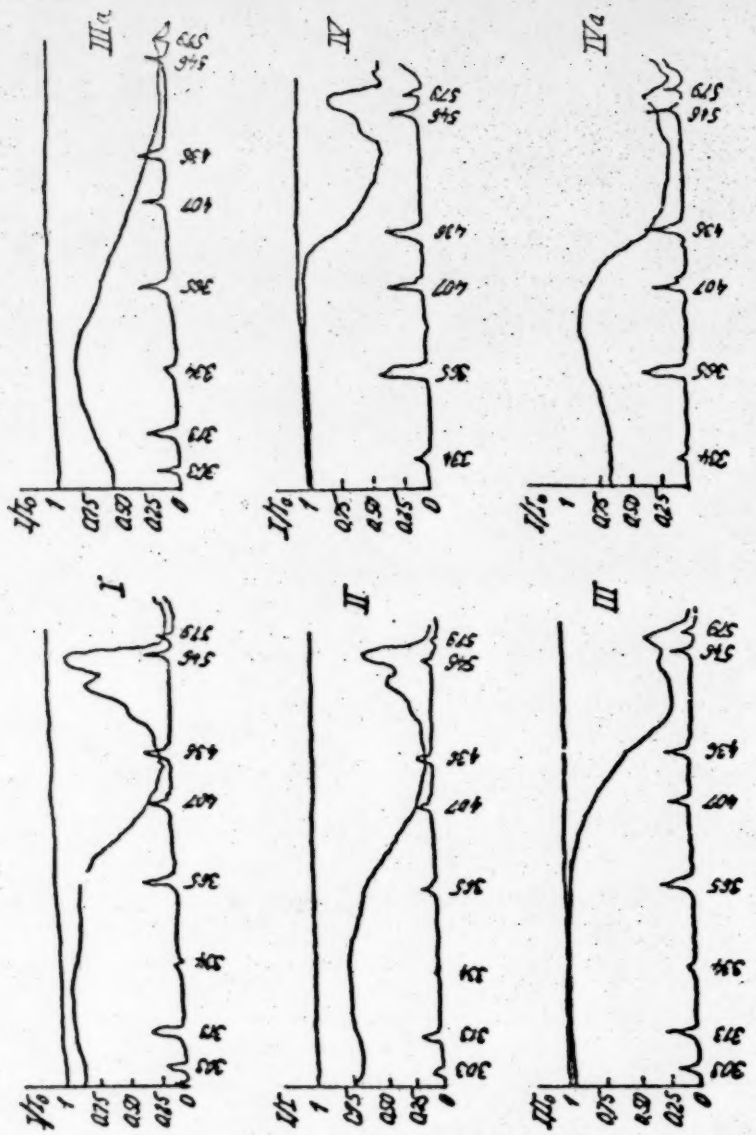


Figure 1.

The properties of the benzopyrilium salts are set forth in Table 1.

The spectrum of benzopyrilium salts in the 579-334 mμ region exhibits a characteristic absorption band in the 579-500 m μ region with an oscillatory structure; this band can clearly serve for identification of benzopyrilium salts. Replacement of the hydrogens in the 6 and 7 position by alkyl and hydroxyl groups shifts the band without changing its character, in this connection we may note that the CH_3 group in the 6-position very slightly shifts the band in the direction of longer waves and that a bigger shift occurs with compounds containing hydroxyl groups in the 6- and 7- positions, although to our surprise no change occurred in the character of the band either on introduction of the OH group or of change in its position. The character of the resultant absorption of benzopyrilium salts is insignificantly affected by the substituents and their position, for I, II and III there are two overlapping bands which are shifted in the direction of longer waves when the hydrogen in position 6 is replaced by methyl and hydroxyl groups, hence for the three bands of compounds I, II and III we observe the same characteristic as for the first band. Introduction of the OH group into the 7- position completely changes the character of the absorption in the 436-334 m μ region, which is fully consistent with our investigations of the absorption spectra of flavylium salts.

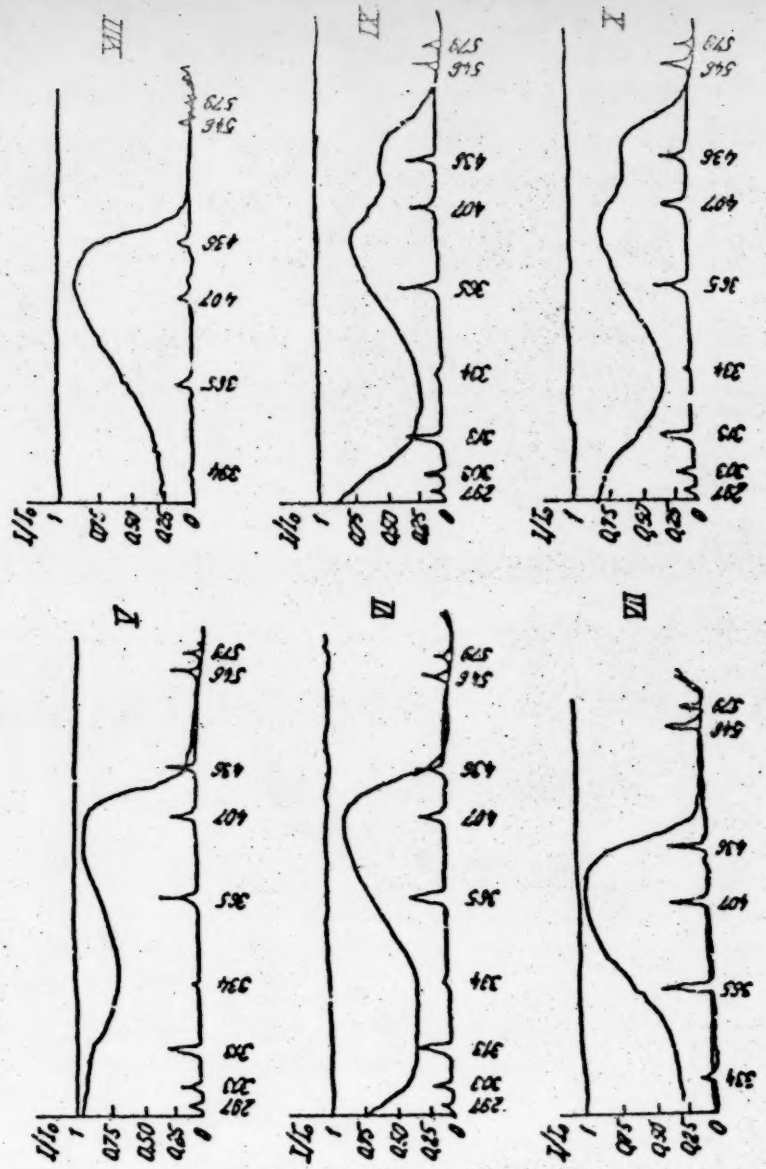


Fig 2.

Flavylium salts

The properties of flavylium salts are set forth in Table 2.

The absorption spectra of the investigated flavylium salts essentially depend upon the character and position of the substituents. Methyl groups in the 6- and 4'-positions and bromine in the 4'-position do not alter the form of the spectrum and only shift it to an insignificant extent in the direction of long waves; a greater effect on the shift is exerted by a substituent in the 4'-position. The form of the absorption curve is completely altered by introducing a hydroxyl group into the molecule, and the position of the hydroxyl group has a significant influence upon the character of the spectrum: Pyrilium salts with a hydroxyl group in the 6-position exhibit two absorption bands and the intensity of absorption of the second is greater than that of the first; substitution of the hydrogen in the 4'-position of 6-hydroxyflavylium ferrichloride leads to the usual shift of the spectrum in the long-wave direction without change of character; the absorption spectrum of 7-hydroxyflavylium ferrichloride also contains two absorption bands, but the intensity of the first is considerably greater than that of the second; substitution of the hydrogen in the 4'-position by bromine and methoxyl leads to the usual shift toward the red without change in the character of the spectrum.

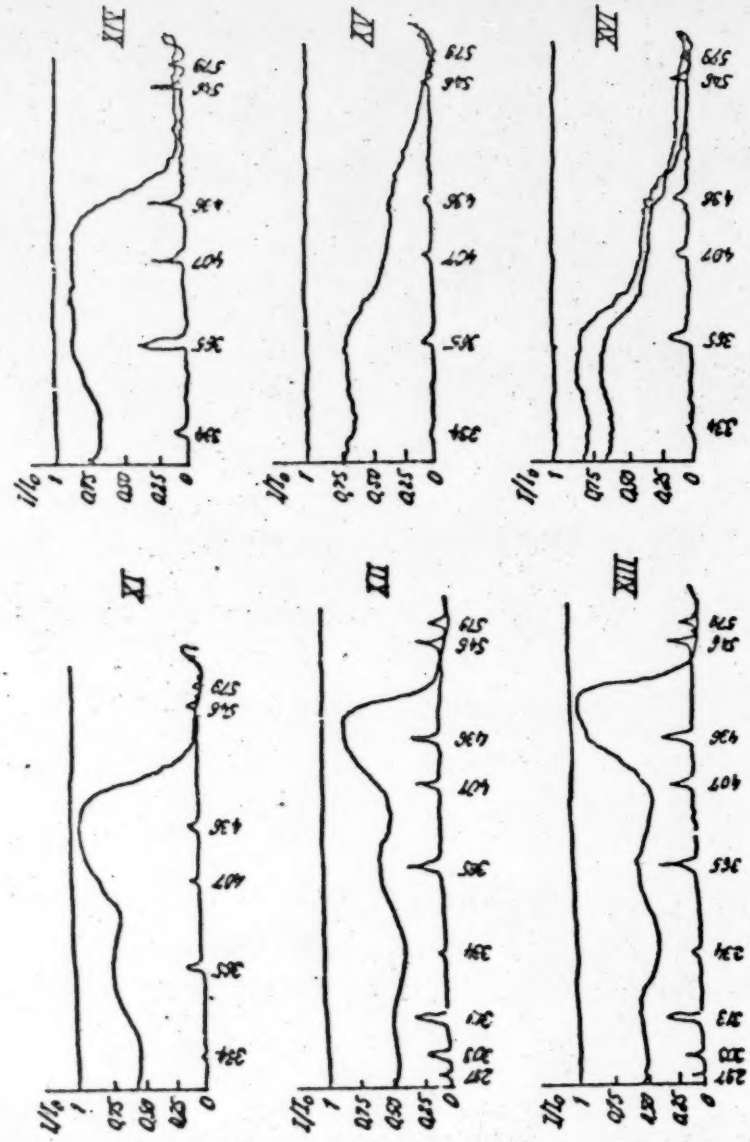


Fig. 3.

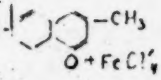
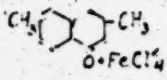
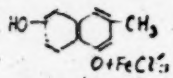
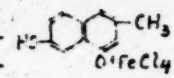
Naphthopyrylium salts

The properties of the naphthopyrylium salts are set forth in Table 3.

We plotted the absorption spectra of naphthopyrylium salts containing alkyl and aryl groups in the 2-position. The character of the absorption depends to a marked extent on the substituent; salts containing alkyl radicals (apart from methyl) have similar spectra whose maxima are shifted more and more toward the red with increasing size of radical (we only measured the maximum of the second conspicuous band); salts with phenyl radicals in the 2-position exhibit in the visible region one conspicuous absorption band whose maximum depends upon the substituent in the phenyl radical and which is shifted toward the red when the hydrogen in the para position is replaced by methyl, bromine, and methoxyl.

The investigated absorption spectra of pyrylium salts depend so characteristically on the structure that they can obviously serve for identification of the respective compounds, and in individual cases also for determination of the position of the substituent (hydroxyflavylium compounds.

TABLE 1

Substance	Formula	Mol. wt.	Color and form	M.p. in deg. C.	Concentration	Thickness of layer (in mm)	λ_{max} in mμ	ε_{max}	Absorption spectrum
1. 2-Methylbenzopyrilium ferrichloride		342.8	Cranberry red	125-125.3	$2.419 \cdot 10^{-4}$	4	545 500 324	$8.78 \cdot 10^{2}$ $5.94 \cdot 10^{2}$ $9.09 \cdot 10^{2}$	I
2. 2,6-Dimethylbenzopyrilium ferrichloride		356.8	Dark-violet needles	103-105	$1.157 \cdot 10^{-4}$	4	548 508 332	$6.37 \cdot 10^{2}$ $4.14 \cdot 10^{2}$ $9.55 \cdot 10^{2}$	II
3. 6-Hydroxy-2-methylbenzopyrilium ferrichloride		358.8	Violet cubes	122-123	$9.42 \cdot 10^{-4}$	4 1	560 516 337	$0.611 \cdot 10^{2}$ $0.452 \cdot 10^{2}$ $7.76 \cdot 10^{2}$	III IIIa
4. 7-Hydroxy-2-methylbenzopyrilium ferrichloride		410.9	Violet needles	145	$3.682 \cdot 10^{-4}$	4 1	570 526 386	$4.27 \cdot 10^{2}$ $2.38 \cdot 10^{2}$ $2.17 \cdot 10^{2}$	IV IVa

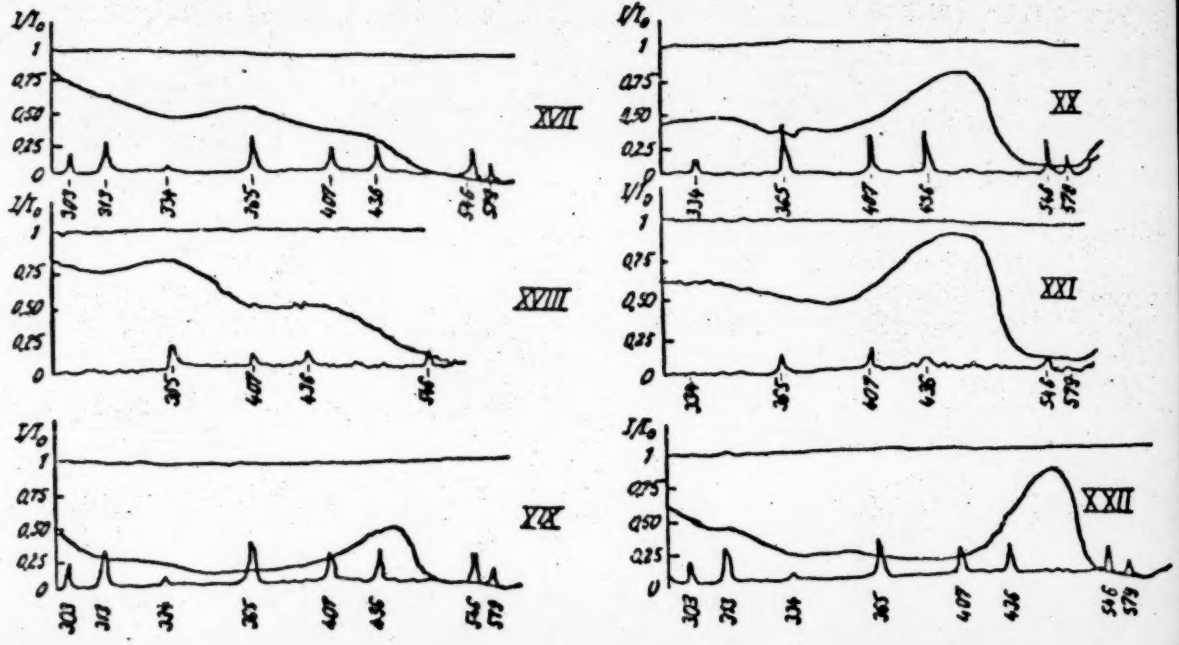
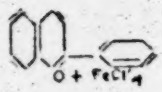
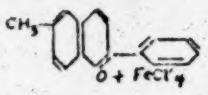
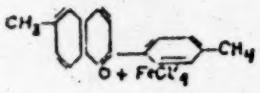
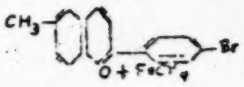
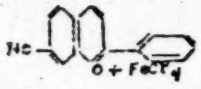
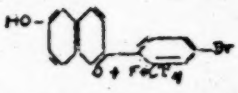
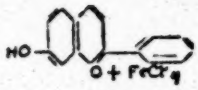
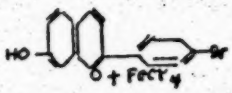
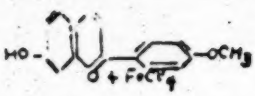
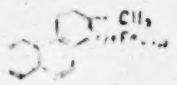
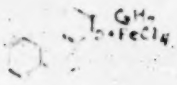
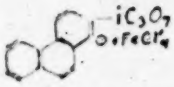
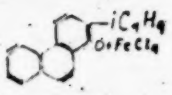
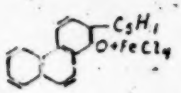
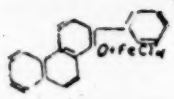
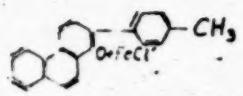
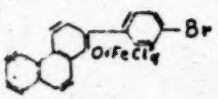
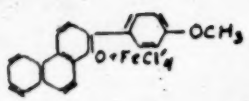
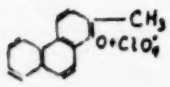


Fig. 4

Substance	Formula	Mol. wt.	Color and form
Flavylium ferrichloride		404.9	Golden-yellow scales
6-Methylflavylium ferrichloride		418.9	Golden-yellow needles
4',6-Dimethylflavylium ferrichloride		439.9	Yellow needles
4'-Bromo-6-methyl-flavylium ferrichloride		497.8	Yellow needles
6-Hydroxyflavylium ferrichloride		420.9	Brown scales
4'-Bromo-6-hydroxy-flavylium ferrichloride		499.8	Brick-brown scales
7-Hydroxyflavylium ferrichloride		420.9	Brown scales
4'-Bromo-7-hydroxy-flavylium ferrichloride		499.9	Orange needles
7-Hydroxy-4'-methoxyflavylium ferrichloride		451.9	Orange needles

M.p. in deg C	Concentration	Thickness of layer (in mm)	λ_{max} in mμ	ϵ_{max}	Absorption spectrum
137-138	$0.972 \cdot 10^{-4}$	4	393	$3.43 \cdot 10^3$	V
170-171.5	$1.856 \cdot 10^{-4}$	4	400	$1.39 \cdot 10^3$	VI
199-200	$0.9374 \cdot 10^{-4}$	4	412	$2.56 \cdot 10^3$	VII
183	$1.695 \cdot 10^{-4}$	2	410	$3.68 \cdot 10^3$	VIII
158-159	$0.687 \cdot 10^{-4}$	4	434 357	$1.13 \cdot 10^2$ $2.11 \cdot 10^3$	IX
190-191.5	$1.038 \cdot 10^{-4}$	2	440 393	$1.87 \cdot 10^3$ $3.04 \cdot 10^3$	X
158-159	$4.088 \cdot 10^{-4}$	1	433 365	$3.26 \cdot 10^2$ $1.42 \cdot 10^3$	XI
169	$0.2519 \cdot 10^{-4}$	1	444 366 312	$3.25 \cdot 10^4$ $1.51 \cdot 10^4$ $1.27 \cdot 10^4$	XII
176-177	$4.23 \cdot 10^{-4}$	1	452 365 316	$3.86 \cdot 10^2$ $8.04 \cdot 10^2$ $8.04 \cdot 10^2$	XIII

TABLE 3

Compound	Formula	Mol. wt.	Color and form
2-Methylnaphthopyrylium ferrichloride		392.9	Dark-green needles
2-Propylnaphthopyrylium ferrichloride		420.9	Light-green scales
2-Isoheptylnaphthopyrylium ferrichloride		420.9	Yellow needles
2-Isobutylnaphthopyrylium ferrichloride		434.9	Yellow scales
2-Amylnaphthopyrylium ferrichloride		449.0	Red-brown scales
2-Phenylnaphthopyrylium ferrichloride		454.9	Orange needles
4-Methyl-2-phenylnaphthopyrylium ferrichloride		468.9	Light-orange needles
4-Bromo-2-phenylnaphthopyrylium ferrichloride		533.88	Orange needles
4-Methoxy-2-phenylnaphthopyrylium ferrichloride		484.9	Red needles
2-Methylnaphthopyrylium perchlorate		294.7	Dark-green crystals

M.p. in °C	Concentration	Thickness of layer (in mm)	λ_{max} in mμ	ϵ_{max}	Absorption spectrum
152	$2.36 \cdot 10^{-4}$	4	366-407	$6.15 \cdot 10^{2}$	XIV
124	$0.309 \cdot 10^{-4}$	2	358	$8.58 \cdot 10^{3}$	XV
100.5 again at 157	$4.12 \cdot 10^{-4}$	2	350	$9.95 \cdot 10^{2}$	XVI
183	$1.29 \cdot 10^{-4}$	4	363	$6.47 \cdot 10^{2}$	XVII
74	$1.72 \cdot 10^{-4}$	4	365	$1.06 \cdot 10^{3}$	XVIII
187.5-188	$0.268 \cdot 10^{-4}$	4	448	$2.80 \cdot 10^{3}$	XIX
166-168	$0.737 \cdot 10^{-4}$	4	457	$0.37 \cdot 10^{2}$	XX
216-217	$1.11 \cdot 10^{-4}$	4	458	$1.55 \cdot 10^{3}$	XXI
206-207	$0.287 \cdot 10^{-4}$	4	474	$4.97 \cdot 10^{2}$	XXII
180	$1.59 \cdot 10^{-5}$	1	407	$8.43 \cdot 10^{3}$	XXIII

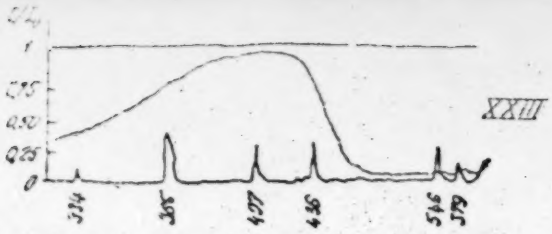


Fig. 5

We express our gratitude to I. V. Obreimov for guidance in the research and to I. A. Palitsyna for assistance in plotting the absorption spectra.

SUMMARY

1. Absorption spectra are plotted of four benzopyrilium, nine flavylium and ten naphthopyrilium salts in the 370-834 mμ region.

2. It was established that the absorption spectrum in the visible region can serve for identification of the structure of a pyrilium salt and in some cases can give information about the position of a substituent.

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* (T.p. = Consultants Bureau Translation Pagination)

DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 2. β-ALKOXY(PHENOXY) VINYLTHIOPHOSPHONYL AND β-ARYLVINYLTHIOPHOSPHONYL CHLORIDES

K. N. Anisimov, N. E. Kolobova and A. N. Nesmeyanov

The alkylthiophosphonyl chlorides have been little investigated. Regarding the chlorides of thiophosphonic acids containing unsaturated radicals, not a single reference to them could be found in the literature. We have developed a perfectly accessible and convenient method of preparation of β-alkoxy(phenoxy)-vinylthiophosphonyl and β-arylvinylthiophosphonyl chlorides. The method starts from crystalline products of addition of phosphorus pentachloride to vinyl ethers ($ROCHCl-CH_2PCl_4\cdot PCl_5$), described in previous communications [1]. These are treated with hydrogen sulfide until the solid substance has been completely transformed into a liquid. The reaction proceeds in one direction with slight evolution of heat without formation of any secondary products and gives yields of over 90%. Reaction scheme:

$$ROCHCl\cdot CH_2PCl_4\cdot PCl_5 + H_2S = ROCH{=}{=}CHPSCl_2 + PSCl_3 + 3HCl.$$

By this method we prepared for the first time the following acid chlorides: β-ethoxyvinylthiophosphonyl chloride; β-isopropoxyvinylthiophosphonyl chloride; β-butoxyvinylthiophosphonyl chloride; β-n-hexoxyvinylthiophosphonyl chloride; β-phenoxyvinylthiophosphonyl chloride; and β-phenylvinylthiophosphonyl chloride. Their physical properties are set forth in the table. The chlorides of β-alkoxy(phenoxy)-vinylthiophosphonic and of β-arylvinylthiophosphonic acids are transparent liquids, readily soluble in common organic solvents, insoluble in water, and stable to hydrolysis. The chlorides of thiophosphonic acids which we prepared differ from the chlorides of β-alkoxy(phenoxy)-vinylthiophosphonic and β-arylvinylphosphonic acids in hardly entering into reaction with alcohols.

Formula	B.p. in °C (p in mm mercury)	n_D^{20}	d_4^{20}	Yield in %
$C_2H_5OCH = CHPSCl_2$	84 (2)	1.5422	1.3334	74
$i\text{-}C_3H_7OCH = CHPSCl_2$	92 (2)	1.5224	1.2684	75
$n\text{-}C_4H_9OCH = CHPSCl_2$	105 (2)	1.5234	1.2471	77
$n\text{-}C_6H_{13}OCH = CHPSCl_2$	128 (2)	1.5255	1.1841	60
$C_6H_5OCH = CHPSCl_2$	130 (1)	1.6086	1.1670	80
$C_6H_5CH = CHPSCl_2$	130 (2)	1.6439	1.3533	91

The boiling points of the β-alkoxy(phenoxy)-vinylphosphonyl chlorides are approximately the same as those of the β-alkoxy(phenoxy)-vinylthiophosphonyl chlorides, but the refractive indices and specific gravities of the β-alkoxy(phenoxy)-vinylthiophosphonyl chlorides are considerably higher than those of the oxygenated derivatives. There is also a difference in the reactivities of the acid chlorides. The β-alkoxy(phenoxy)-vinylphosphonyl chlorides are more reactive in chlorine exchange reaction than are the β-alkoxy(phenoxy)-vinylthiophosphonyl chlorides.

EXPERIMENTAL

β-Ethoxyvinylthiophosphonyl chloride $C_2H_5OCH = CHPSCl_2$. Into a three-necked flask fitted with mechanical stirrer, reflux condenser and dropping funnel were charged 300 ml dry benzene and 83 g PCl_5. Dropwise addition was made to the resultant suspension of 14.2 g vinylethyl ether dissolved in 15 ml benzene. Crystals separated during the addition of the ether, and after the whole amount of ether had been added a copious

crystalline precipitate had formed. The next day the latter was heated on a water bath with stirring at 60-65° for 30 min. After cooling, dry hydrogen sulfide was passed through. Hydrogen chloride was evolved during this process and heat was released by the reaction mass. The addition product was gradually converted into the thiophosphonyl chloride. Gas was passed through until the precipitate had completely dissolved and the liquid had cooled. After distilling off the benzene and phosphorus thiochloride, the residue was kept on a boiling water bath in the vacuum of a water pump for about an hour and then fractionated at 2 mm to give 30 g substance (74% of the theoretical): b.p. 84° (2 mm); n_D^{25} 1.5422; d_4^{25} 1.3334.

Found %: C 23.76, 23.73; H 3.65, 3.75; P 14.99; 15.12
$C_4H_7OPSCl_2$. Calculated %: C 23.41; H 3.41; P 15.11

β-Ethoxyvinylthiophosphonyl chloride is a pale-yellow liquid, stable to hydrolysis by water; it is non-reactive at room temperature with alcohols, soluble in common organic solvents.

β-Isopropoxyvinylthiophosphonyl chloride $i\text{-}C_3H_7OCH = CHPSCl_2$. To a suspension of 83 g PCl_5 in 250 ml dry benzene was gradually added, with energetic stirring, 12.2 g vinylisopropyl ether in 15 ml benzene; the reaction mass was then worked up as above. Yield 33 g (75% of the theoretical), b.p. 92° (2 mm); n_D^{25} 1.5224; d_4^{25} 1.2964

Found %: C 27.52, 27.60; H 3.96, 3.82; P 14.02, 14.04
$C_5H_9OPSCl_2$. Calculated %: C 27.39; H 4.10; P 14.15

β-Isopropoxyvinylthiophosphonyl chloride is an easily distillable liquid with the characteristic odor of an acid chloride; its properties resemble those of the preceding substance.

β-n-Butoxyvinylthiophosphonyl chloride $n\text{-}C_4H_9OCH = CHPSCl_2$. 20 g vinylbutyl ether, dissolved in an equal volume of benzene, was run with stirring into a suspension of 83 g PCl_5 in 300 ml dry benzene. After passing in hydrogen sulfide and driving off the solvent and the phosphorus thiochloride, β-n-butoxyvinylthiophosphonyl chloride was isolated in a yield of 36 g (77% of the theoretical), b.p. 105° (2 mm); n_D^{25} 1.5234; d_4^{25} 1.2471.

Found %: Cl 30.55, 30.61; P 13.25, 13.29; C 31.36, 31.45; H 4.87; 4.94
$C_6H_{11}OPSCl_2$. Calculated %: Cl 30.47; P 13.30; C 30.90; H 4.72

This acid chloride is a readily mobile liquid with the properties usual for substances of this class.

β-n-Hexoxyvinylthiophosphonyl chloride $n\text{-}C_6H_{13}OCH = CHPSCl_2$. 47 g finely pulverized PCl_5 and 150 ml benzene were placed in a flask. Addition was made with stirring of 12.8 g vinylhexyl ether dissolved in an equal volume of benzene. After treatment with hydrogen sulfide and removal of the benzene and phosphorus thiochloride there was isolated 13.6 g (60% of the theoretical) of the acid chloride. β-n-Hexoxyvinylthiophosphonyl chloride has b.p. 128° (2 mm), n_D^{25} 1.5255; d_4^{25} 1.1841; usual properties.

Found %: C 38.12, 37.80; H 3.00, 2.87; P 37.94, 12.05; 12.07; H 2.76;
$C_8H_{15}OPSCl_2$. Calculated %: C 37.94; H 2.76; P 12.25.

β-Phenoxyvinylthiophosphonyl chloride $C_6H_5OCH = CHPSCl_2$. Into a suspension of PCl_5 prepared from 83 g PCl_5 and 250 ml benzene was slowly run 24 g vinylphenyl ether. Hydrogen sulfide was passed through the resultant crystalline product, after which the reaction product was worked up in the usual way. Yield 40 g acid chloride; b.p. 140° (4 mm); n_D^{25} 1.6086; d_4^{25} 1.1670.

Found %: C 38.12, 37.86; H 3.00; 2.87; P 37.94; 12.05, 12.07; H 2.76;
$C_8H_7OPSCl_2$. Calculated %: C 37.94; H 2.76; P 12.25. Usual properties.

β-Phenylvinylthiophosphonyl chloride $C_6H_5CH = CHPSCl_2$. 20.8 g freshly distilled dry styrene dissolved in 20 ml benzene was added in several portions to 83 g finely pulverized PCl_5 in 250 ml benzene. After the whole of the styrene had been added, the reaction mass was thoroughly stirred and left overnight. The next day the mass was heated on a water bath at 65-70° for 30 minutes before passing a stream of dry hydrogen sulfide until the precipitate had completely dissolved and the resultant liquid had cooled. After driving off the benzene and the phosphorus thiochloride, the residue was kept in the vacuum of a water jet pump on a boiling water bath for an hour. Yield 43.5 g substance (91% of the theoretical), b.p. 130° (2 mm); n_D^{25} 1.6439; d_4^{25} 1.3533.

Found %: C 40.30, 40.12; H 3.28, 3.22; P 13.08; 13.02
$C_8H_7OPSCl_2$ Calculated %: C 40.50; H 2.95; P 13.12

The properties were the same as those of the other β-alkoxyvinylthiophosphonyl chlorides which have been described.

SUMMARY

1. A simple and convenient method was developed for the synthesis of chlorides of β-alkoxy(phenoxy)-vinylthiophosphonic and β-arylvinylthiophosphonic acids by reaction of the products of addition of PCl_5 to vinyl ethers with hydrogen sulfide.

2. The following acid chlorides were prepared and characterized: β-ethoxyvinylthiophosphonyl chloride; β-isopropoxyvinylthiophosphonyl chloride; β-n-butoxyvinylthiophosphonyl chloride; β-n-hexoxyvinylthiophosphonyl chloride; β-phenoxyvinylthiophosphonyl chloride; and β-phenylvinylthiophosphonyl chloride.

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DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 3. β-ALKOXYETHOXYVINYLPHOSPHONYL AND β-ALKOXYETHOXYVINYLTHIOPHOSPHONYL CHLORIDES

K. N. Anisimov, N. E. Kolobova and A. N. Nesmeyanov

In our preceding communications [1] methods were described for the synthesis of β-alkoxyvinylphosphonyl and β-alkoxyvinylthiophosphonyl chlorides by addition of PCl_5 to vinyl ethers. In the present research we investigated the reaction of PCl_5 with monoalkylvinyl ethers of ethylene glycol (the methylvinyl, ethyl vinyl and n-butylvinyl ethers).

Considerable heat was developed and much hydrogen chloride was evolved on reacting the monoalkylvinyl ethers of ethylene glycol with PCl_5 in benzene. At the end of the reaction a yellowish oily layer was formed which after cooling changed into a dense crystalline mass – the product of addition of two molecules of PCl_5 to a molecule of monoalkylvinyl ether of ethylene glycol.

The following addition products were prepared in the above conditions:

$CH_3-O-CH_2-CH_2-O-CHCl-CH_2\cdot PCl_4\cdot PCl_5$. (1)

$C_2H_5-O-CH_2-CH_2-O-CHCl-CH_2\cdot PCl_4\cdot PCl_5$ (2)

$n\text{-}C_4H_9-O-CH_2-CH_2-O-CHCl-CH_2\cdot PCl_4\cdot PCl_5$. (3)

These were not isolated due to their ease of hydrolysis, and also due to the release of hydrogen chloride both while the reaction was being carried out and on standing.

Without separation from the reaction mixture, these substances were subjected to the action of sulfur dioxide and hydrogen sulfide. Introduction of sulfur dioxide caused heat to be liberated and hydrogen chloride came off, while the crystalline mass was gradually transformed into a liquid. When the whole mass had changed into liquid, the reaction was stopped. The β-alkoxyethoxyvinylphosphonyl chlorides were isolated from this liquid by fractionation.

In a general way the reaction leading to formation of the acid chlorides may be represented by the scheme:

$$ROCH_2-CH_2-O-CHCl-CH_2\cdot PCl_4\cdot PCl_5 + 2SO_2 \rightarrow$$

$$\rightarrow ROCH_2-CH_2-O-CH=CHPOCl_2 + 2SOCl_2 + POCl_3 + HCl$$

The same acid chlorides were synthesized by the action of water and carboxylic acids upon the products of addition of PCl_5 to monoalkylvinyl ethers of ethylene glycol according to the equations:

$$ROCH_2-CH_2-O-CHCl-CH_2\cdot PCl_4\cdot PCl_5 + 2H_2O \rightarrow$$

$$\rightarrow ROCH_2-CH_2-O-CH=CHPOCl_2 + POCl_3 + 5HCl$$

$$ROCH_2-CH_2-O-CHCl-CH_2\cdot PCl_4\cdot PCl_5 + 2CH_3COOH \rightarrow$$

$$\rightarrow ROCH_2-CH_2-O-CH=CH\cdot POCl_2 + POCl_3 + 2CH_3COCl + 3HCl.$$

β-Alkoxyethoxyvinylphosphonyl chlorides are colorless, transparent liquids, easily distillable in vacuum, rapidly decolorizing bromine water and permanganate, and hydrolyzable by water with formation of non-distillable and non-crystallizing syrups; the chlorides are soluble in all organic solvents. By this method the following compounds were prepared in yields of 90-97% of the theoretical: The chlorides of β-methoxy ethoxyvinylphosphonic, and β-ethoxyethoxyvinylphosphonic, and β-n-butoxyethoxyvinylphosphonic acids.

The β-alkoxyethoxyvinylthiophosphonyl chlorides were prepared in the same conditions as for the synthesis of the β-alkoxyethoxyvinylphosphonyl chlorides. The only difference was that the action of hydrogen sulfide on the products of addition of PCl_5 to the monoalkylvinyl ethers was continued up to full transformation of the crystalline product into a liquid. After driving off the solvent and phosphorus thiochloride, the β-alkoxyethoxyvinylthiophosphonyl chlorides were isolated. Reaction scheme:

$$ROCH_2-CH_2-O-CHCl-CH_2PCl_4\cdot PCl_5 + 2H_2S \rightarrow$$
$$\rightarrow ROCH_2-CH_2-O-CH=CHPSCl_2 + PSCl_3 + 5HCl.$$

The chlorides of β-methoxyethoxyvinylthiophosphonic and β-n-butoxyethoxyvinylthiophosphonic acids were isolated in a yield of 76-86 % of the theoretical. The chlorides of β-alkoxyethoxyvinylthiophosphonic acids are pale-yellow liquids; they rapidly decolorize bromine water and permanganate and give a positive reaction for chlorine; they are hydrolyzed very slowly by water; they are easily soluble in common organic solvents. The constants and yields of the prepared β-alkoxyethoxyvinylphosphonyl and β-alkoxyethoxyvinylthiophosphonyl chlorides are set forth in the table.

Formula	B.p. in °C (p in mm mercury)	n_D^{20}	d_4^{20}	Yield in %
$CH_3O-CH_2-CH_2-O-CH=CHPOCl_2$	115 (2)	1.4991	1.3200	95
$C_2H_5O-CH_2-CH_2-O-CH=CHPOCl_2$	123 (2)	1.4920	1.2881	97
$n-C_4H_9O-CH_2-CH_2-O-CH=CHPOCl_2$	142 (2)	1.4869	1.2133	90
$CH_3O-CH_2-CH_2-O-CH=CHPSCl_2$	113 (2)	1.5413	1.3364	76
$C_2H_5O-CH_2-CH_2-OCH=CHPSCl_2$	120 (2)	1.5330	1.2887	85
$n-C_4H_9O-CH_2-CH_2-OCH=CHPSCl_2$	137 (2)	1.5100	1.2210	86

EXPERIMENTAL

β-Methoxyethoxyvinylphosphonyl chloride $CH_3-O-CH_2-CH_2-O-CH=CHPOCl_2$. In a three-necked flask, fitted with mechanical stirrer, reflux condenser (with calcium chloride tube) and dropping funnel, were placed 150 ml dry benzene and 83.5 g (0.4 mole) finely pulverized PCl_5. With energetic stirring of the suspension, gradual addition was then made of 20.4 g (0.2 mole) benzene solution of ethylene glycol methylvinyl ether (b.p. 107.5 deg; n_D^{20} 1.4162), prepared by the method of Shostakovsky and Tyupaev [2]. Addition of ether was accompanied by heat liberation and by copious evolution of hydrogen chloride. After the whole amount of the ether had been added, the mixture formed two layers – the upper one of benzene and the lower one of an oily liquid. The latter crystallized completely after cooling. The next day, after heating for 30 min on a water bath at 55-60°, the mixture was treated with sulfur dioxide until the crystalline mass had completely dissolved. The benzene, phosphorus oxychloride and thionyl chloride were driven off in the vacuum of a water jet pump. Fractionation of the residue yielded 42 g substance (95 % of the theoretical) with b.p. 115° (2 mm); n_D^{20} 1.4991; d_4^{20} 1.3200.

Found %	C 26.92; 27.20,	H 4.27; 4.32;	P 14.11; 14.17,	Cl 32.61; 32.57	
$C_3H_5O_3PCl_2$. Calculated %	C 27.39,	H 4.10,	P 14.15;	Cl 32.42	

β-Ethoxyethoxyvinylphosphonyl chloride $C_2H_5-O-CH_2-CH_2-O-CH=CHPOCl_2$. 24 g (0.2 mole) ethylene glycol monoethylvinyl ether (b.p. 123.7 deg; n_D^{20} 1.4014) was added with stirring to 83.5 g PCl_5 dissolved in 150 ml benzene. The following day the addition product was treated with sulfur dioxide until the crystalline product had changed into a liquid. Fractionation of the reaction mass yielded 46 g substance (97 % of the theoretical) with b.p. 123 deg (2 mm); n_D^{20} 1.4920; d_4^{20} 1.2881.

Found %	C 30.88; 30.84,	H 4.65; 4.88,	P 13.59, 13.44,	Cl 30.43, 30.54	
$C_4H_7O_3PCl_2$. Calculated %	C 30.90;	H 4.72,	P 13.30;	Cl 30.47	

β-n-Butoxyethoxyvinylphosphonyl chloride $n-C_4H_9-O-CH_2-CH_2-O-CH=CHPOCl_2$. 28.8 g (0.2 mole) ethylene glycol monobutylvinyl ether was added with stirring to a benzene suspension of PCl_5 consisting of 83.5 g PCl_5 and 150 ml benzene. The crystalline addition product was treated with sulfur dioxide until the whole of the crystalline mass had changed into liquid. Vacuum fractionation yielded 46.9 g acid chloride (90 % of the theoretical) with b.p. 142° (2 mm); n_D^{20} 1.4869; d_4^{20} 1.2133.

Found %	P 11.82, 11.87;	Cl 27.20; 27.47	
$C_6H_{11}O_3PCl_2$. Calculated %	P 11.87;	Cl 27.20	

β-Methoxyethoxyvinylthiophosphonyl chloride $CH_3-O-CH_2-CH_2-O-CH=CHPSCl_2$. The synthesis was performed in the above-described apparatus. To a benzene suspension comprising 83 g PCl_5 and 150 ml benzene was added with stirring 20 g (0.2 mole) ethylene glycol monomethylvinyl ether (b.p. 107.5°; n_D^{20} 1.4162). The addition product was subjected to the action of hydrogen sulfide until the whole of the crystalline material had changed into liquid. Fractionation yielded 35.5 g substance (76 % of the theoretical) with b.p. 113° (2 mm); n_D^{20} 1.5413; d_4^{20} 1.3364.

Found %: C 25.82, 26.02, H 3.44; 3.75; P 12.89; 13.16

$C_3H_9O_2PSCl_2$. Calculated %: C 25.53; H 3.82; P 13.19

β-Ethoxyethoxyvinylthiophosphonyl chloride $C_2H_5-O-CH_2-CH_2-O-CH=CHPSCl_2$. 23.2 g (0.2 mole) ethylene glycol monoethyl vinyl ether (b.p. 123.7 °; n_D^{20} 1.4104) was added to a suspension of 82.5 g PCl_5 in 130 ml benzene. The following day the crystalline addition product was treated with hydrogen sulfide until the whole of the crystalline mass had changed into liquid. Vacuum fractionation yielded 42.6 g substance (85 % of the theoretical) with b.p. 120 deg (2 mm); n_D^{20} 1.5330, d_4^{20} 1.2887.

Found %: C 29.10; 29.19, H 4.16; 3.94; P 12.55; 12.46

$C_4H_{11}O_2PSCl_2$. Calculated %: C 28.91; H 4.41; P 12.44

β-n-Butoxyethoxyvinylthiophosphonyl chloride $n\text{-}C_4H_9-O-CH_2-CH_2-O-CH=CHPSCl_2$. To 83 g (0.4 mole) PCl_5 and 150 ml benzene was added, with stirring, 28.8 g ethylene glycol n-butylvinyl ether (b.p. 159-160°; n_D^{20} 1.4210). The following day the crystalline addition product was treated with hydrogen sulfide. Fractionation in vacuum yielded 47 g substance (86% of the theoretical) with b.p. 137 ° (2 mm), n_D^{20} 1.5100, d_4^{20} 1.2210.

SUMMARY

Reaction of PCl_5 with alkylvinyl ethers of ethylene glycol yielded the chlorides of: β-methoxyethoxyvinylphosphonic, β-ethoxyethoxyvinylphosphonic, and β-n-butoxyethoxyvinylphosphonic acids, also the chlorides of β-methoxyethoxyvinylthiophosphonic, β-ethoxyethoxyvinylthiophosphonic and β-n-butoxyethoxyvinylthiophosphonic acids.

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DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 4. ARYLVINYLPHOSPHONYL CHLORIDES

K. N. Anisimov

We have previously described the reaction of addition of phosphorus pentachloride to vinyl ethers and the synthesis of β-alkoxy(phenoxy)-vinylphosphonyl chlorides [1]. We made a similar investigation of unsaturated compounds of the aromatic series - styrene, indene and phenylacetylene. As is known, Harnist [2] added phosphorus pentachloride to styrene, diphenylethylene, isobutylene and phenylacetylene. Bulle reacted phosphorus pentachloride with indene [3]. Bergman and Bondi [4,5,6,7] studied the addition of phosphorus pentachloride to unsaturated compounds of the aromatic series.

All these investigators subjected to hydrolysis the products of addition of phosphorus pentachloride to unsaturated hydrocarbons and obtained unsaturated phosphonic acids. They did not carry out other investigations with the addition products.

On the basis of our research we concluded that if the products of addition of phosphorus pentachloride to styrene, phenylacetylene, and indene were to be reacted with sulfur dioxide, formation should take place of the corresponding chlorides of the unsaturated phosphonic acids which can serve as starting materials for the synthesis of diverse derivatives of unsaturated phosphonic acids. The first experiments showed the correctness of our conclusion. Reactions were performed in the following conditions. In an Erlenmeyer flask were placed dry benzene and thoroughly pulverized phosphorus pentachloride, the flask was then closed with a cork through which was inserted a calcium chloride tube and a dropping funnel. The unsaturated compound was added in portions from the dropping funnel with stirring. The reaction took place with liberation of heat and with evolution of hydrogen chloride. At the end of the reaction, a crystalline mass had formed and this was left overnight. The following day the addition product was treated with sulfur dioxide until the solid mass was completely changed into a liquid. The benzene was then driven off and the residue was at first kept in the vacuum of a water jet pump on a water bath until the hydrogen chloride had been completely removed, and then fractionated in vacuum.

In this way β-phenylvinylphosphonyl chloride was obtained in a yield of 98-99% of the theoretical, and indenyl-2-phosphonyl chloride in slightly lower yield. The synthesized acid chlorides are crystalline substances with an acid chloride odor, readily soluble in ether, chloroform, benzene and other organic solvents; they react slowly with cold water.

The preparation of the chlorides of arylvinylphosphonic acids may be expressed by the scheme:

$$RCH{=}CH_2 + 2PCl_5 \rightarrow RCHCl-CH_2PCl_4\cdot PCl_5.$$

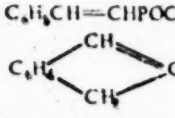
$$RCHCl-CH_2PCl_4\cdot PCl_5 + 2SO \rightarrow RCH{=}CHPOCl_2 + POCl_3 + 2SOCl_2 + HCl.$$

β-Chlorophenylvinylphosphonyl chloride is obtained in quantitative yield by the same method as described above, except that hydrogen chloride was not split off from the product of addition of phosphorus pentachloride to phenylacetylene. β-Chlorophenylvinylphosphonyl chloride is a thick, transparent liquid, soluble in common organic solvents, slowly hydrolyzed by cold water and more energetically by hot. The synthesis of β-chlorophenylvinylphosphonyl chloride may be represented by the equations:

$$C_6H_5C{\equiv}CH + 2PCl_5 \rightarrow C_6H_5CCl{=}CHPCl_4\cdot PCl_5.$$

$$C_6H_5CCl{=}CH_2PCl_4\cdot PCl_5 + 2SO_2 \rightarrow C_6H_5CCl{=}CHPOCl_2 + POCl_3 + 2SOCl_2.$$

β-Arylvinylphosphonyl chlorides were also prepared in this investigation, using the calculated amount of water in place of sulfur dioxide. The constants and yields of the prepared acid chlorides are set forth in the table.

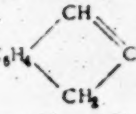
Formula	B.p. in °C (p in mm mercury column)	n_D^{20}	d_4^{20}	Yield in %
$C_6H_5CH{=}CHPOCl_2$	M.p. 71-72°	—	—	96
	M.p. 73-74°	—	—	62
$C_6H_5CCl{=}CHPOCl_2$	142.5-143.5° (1)	1.6175	1.4675	80

EXPERIMENTAL

β-Phenylvinylphosphonyl chloride $C_6H_5CH{=}CHPOCl_2$. To 104 g phosphorus pentachloride in 150 ml dry benzene was gradually added, with stirring and water cooling, 26.2 g styrene dissolved in 50 ml benzene. A portion of the styrene resulted in formation of a dense crystalline mass. The next day a stream of sulfur dioxide was passed into the reaction mixture until the crystalline mass had completely changed into liquid. Hydrogen chloride was copiously evolved by the reaction mixture during introduction of the sulfur dioxide. The mixture was then subjected to vacuum fractionation to give 55 g (96% of the theoretical) of acid chloride: b.p. 139° (2 mm); M.p. 71-72°.

	Found %:	C 43.30, 43.19;	H 3.28, 3.32;	Cl 31.86, 32.20.
$C_8H_7OCl_2P$.	Calculated %:	C 43.43;	H 3.15;	Cl 32.12

β-Phenylvinylphosphonyl chloride is a white crystalline substance with an acid chloride odor, soluble in ordinary organic solvents and slowly hydrolyzing in water.

Indenyl-2-phosphonyl chloride  In a three-necked flask, fitted with stirrer, reflux condenser and dropping funnel, were placed 200 ml dry benzene and 83 g finely pulverized phosphorus pentachloride. To the suspension was added 24 g indene with energetic stirring dissolved in 20 ml benzene. A voluminous crystalline mass had formed when the whole of the indene had been added. The following day a further 50 ml benzene was added, the whole was stirred and heated to 65-70°; then a stream of sulfur dioxide was then passed through until the crystalline mass had been completely changed into liquid. After the benzene, phosphorus oxychloride and thionyl chloride had been driven off, the residue was kept on a boiling water bath in the vacuum of a water jet pump for removal of the hydrogen chloride. Vacuum fractionation of the residue yielded 30 g (62% of the theoretical) substance with b.p. 133 deg (1 mm); M.p. 73-74°.

	Found %:	C 46.14, 46.41;	H 2.99, 3.20;	P 13.22, 13.12
$C_9H_7OCl_2P$	Calculated %:	C 46.35;	H 3.00	P 13.30

Indenyl-2-phosphonyl chloride is readily soluble in many organic solvents, and is slowly hydrolyzed by water.

β-Chlorophenylvinylphosphonyl chloride $C_6H_5CCl{=}CHPOCl_2$. To a suspension of 83 g phosphorus pentachloride in 150 ml dry benzene was gradually added 20.4 g phenylacetylene with shaking and water cooling. Heat was developed during the reaction. The following day sulfur dioxide was passed into the crystalline mass until the latter was completely transformed into a liquid. The mixture was then fractionated in vacuum. The solvent, phosphorus oxychloride and thionyl chloride were driven off in a low vacuum (water jet pump) and the residue twice fractionated at 1 mm. Yield 44.5 g (87% of the theoretical) of β-chlorophenylvinylphosphonyl chloride with b.p. of 142.5-143.5° (1 mm); n_D^{20} 1.6175, d_4^{20} 1.4675.

	Found %:	P 12.11, 12.40;	C 37.44, 37.21;	H 2.67, 2.40;	Cl 41.53, 41.40
$C_8H_6OPCl_3$.	Calculated %:	P 12.15;	C 37.57;	H 2.34;	Cl 41.68

β-Chlorophenylvinylphosphonyl chloride is a colorless, viscous liquid, faintly fuming in the air, slowly hydrolyzed by water. It has the odor of an acid chloride and is soluble in many organic solvents.

SUMMARY

For the first time a method was developed for the preparation of chlorides of β-arylvinylphosphonic acids.

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[6] E. Bergmann, A. Bondi, Ber., 63, 377 (1930).

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SYNTHESIS OF ESTERS OF PHOSPHONIC ACIDS CONTAINING HETEROCYCLIC RADICALS

COMMUNICATION 4. ESTERS OF PHOSPHONIC ACIDS CONTAINING ISOXAZOLE AND QUINOXALINE RADICALS

B. A. Arbuzov and V. M. Zoroastrova

In previous communications we described the results of syntheses of esters of phosphonic acids containing thiazole radicals [1], heterocyclic radicals with one and two atoms of oxygen in the ring [2], and the piperidine radical [3]. In a continuation of these investigations we have studied esters of phosphonic acids containing other heterocycles. In the present paper we present data for the synthesis of esters of phosphonic acids containing isoxazole and quinoxaline radicals.

Action of triethylphosphite upon 3-chloromethylisoxazole at 150-155° gave the ethyl ester of 3-isoxazolylmethylphosphonic acid in the form of a viscous, colorless liquid in the yield of 59.1% of the theoretical, b.p. 152-153° (7-7.5 mm); d_4^{20} 1.1862, n_D^{20} 1.4659. Found MR 50.93. Calculated MR 50.72.

Reaction of molar amounts of trimethyl phosphite and 3-chloromethyl soxazole gave in lower yield (24% of the theoretical) the methyl ester of 3-isoxazolylmethylphosphonic acid with b.p. 142-145° (5 mm); d_4^{20} 1.2744, n_D^{20} 1.4670. Found MR 41.64. Calculated MR 41.49.

Similarly from tri-n-propylphosphite and 3-chloromethylisoxazole at about 160° was obtained n-propyl 3-isoxazolylmethanephosphonate with b.p. 150-152° (2.5 mm). d_4^{20} 1.1541; n_D^{20} 1.4675. Found MR 59.47; Calculated MR 59.95. Yield 65.5%.

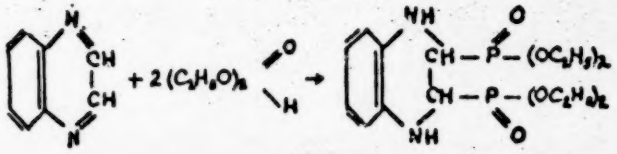
Ethyl 3-isoxazolylmethanephosphonate was obtained by the action of sodium diethylphosphite on 3-chloromethylisoxazole. The yield of ester obtained by this method was considerably lower than the yield of ester obtained by reaction of triethyl phosphite with 3-chloromethylisoxazole and was 17% of the theoretical.

The esters of 3-isoxazolylmethanephosphonic acid are viscous liquids soluble in ether, benzene, alcohol and water. An attempt to prepare the free 3-isoxazolylphosphonic acid by hydrolysis of the ester with hydrochloric acid (1:1) was unsuccessful due to resinification of the products. Alkaline hydrolysis of the esters gave the phosphonic acid in the form of a viscous, non-crystallizing syrup, from which the barium salt was subsequently prepared. The second part of the research was devoted to the study of the reaction of trialkyl phosphites with halogenated derivatives of quinoxaline.

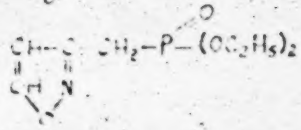
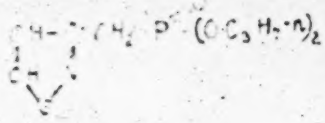
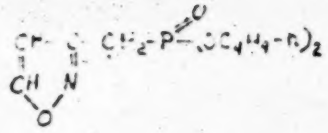
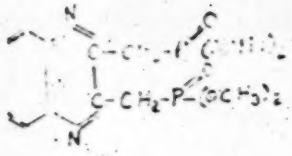
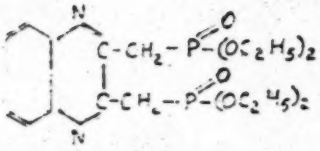
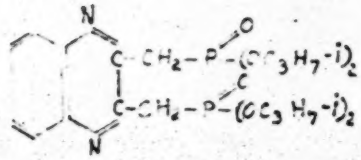
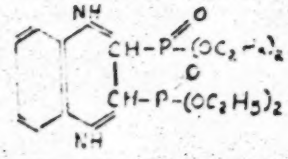
Condensation of dibromodiacetyl with o-phenylenediamine in ethanolic solution gave 2,3-di(ω-bromomethyl)-quinoxaline. Reaction of the latter with trimethyl, triethyl and triisopropyl phosphites enabled synthesis of the corresponding esters of 2,3-di(ω-phosphonomethyl)-quinoxaline. All the esters are crystalline substances, soluble in organic solvents and in water. Saponification of the esters gave the free acid. It is interesting to note that on acting with sodium diethyl phosphite on 2,3-di(ω-bromomethyl)-quinoxaline, the anticipated reaction product was not isolated. The constants of the prepared esters of phosphonic acids are set forth in the table.

The above method can serve for the preparation of esters of phosphonic acids containing the phosphonic group in the side chain. For the preparation of esters of phosphonic acids containing the phosphonic group directly attached to a heterocyclic nucleus, we made use of Pudovik's method of addition of dialkyl phosphorous acids at the active double bond.

It is known from literature data that quinoxaline adds on at the C=N bond [4]. By analogy, therefore, we should expect diethyl phosphorous acid to add on in this way to quinoxaline.



TABLE

Prep. No.	Formula	B.p. in °C (p in mm mercury)	d_0^{20}	n_D^{20}	MR Found	MR Calculate
1		142-145 (5)	1.2744	1.4670	41.60	41.49
2		152-153 (7-7.5)	1.1892	1.4650	50.93	50.72
3		150-152 (2.5)	1.1541	1.4675	54.49	69.20
4		155-156 (1)	1.0750	1.4575	69.77	69.20
5		M.p. 115-116	Colorless prisms from ether			
6		92-93	From n-heptane			
7		102-103	From n-heptane			
8		168-170				

Experiments were carried out which confirmed this expectation. Under the influence of sodium ethoxide, sodium diethyl phosphite adds on to quinoxaline in the ratio of 2 moles to 1 mole. The addition product, 1,4-dihydro-2,3-di(diethylphosphono)-quinoxaline, is a crystalline substance with m.p. 168-170°. Substitution of the hydrogens in the 2-and 3-positions of quinoxaline by methyl groups hinders the addition of diethylphosphorous acid, and the reaction does not take place.

EXPERIMENTAL

1. Action of 3-chloromethyl soxazole on triethyl phosphite. 10 g triethyl phosphite was placed in a small Arbuzov flask and heated on an oil bath to 120-125° inside a small flask. Dropwise addition was made to the heated triethyl phosphite of 7.01 g (1 mole per mole triethyl phosphite) 3-chloromethylisoxazole, the heating being gradually intensified during the operation. Reaction commenced at 150-155° (evolution of ethyl chloride). This temperature was maintained for an hour. The volume of the reaction mixture gradually contracted. Vacuum distillation yielded 7.8 g (59% of the theoretical) of product boiling at 152-153° (7-7.5 mm); d_4^{20} 1.1892; n_D^{20} 1.4640; Found MR 50.93; calculated MR 50.72. The colorless, fairly viscous liquid is soluble in ether, benzene, ethanol and water.

Found %: P 11.14;
Calculated %: P 11.14 $C_8H_{14}O_4PN$

2. Action of 3-chloromethyl soxazole on trimethyl phosphite. The reaction procedure was similar to that described above. Reactants were 6.3 g trimethyl phosphite and 5.83 g 3-chloromethylisoxazole. The trimethyl phosphite which distilled over was returned to the reaction mixture. After heating for an hour, the reaction products were fractionated in vacuum to give 2 g (22%) viscous, faint yellow liquid. Further heating led to serious decomposition of the reaction product. B.p. 142-145° (5 mm); d_4^{20} 1.2744; n_D^{20} 1.4670; Found MR 41.60, calculated MR 41.49. The product dissolves readily in organic solvents. Unlike the first product it is also easily soluble in water.

Found %: P 15.73
Calculated %: P 16.22. $C_6H_{11}O_4PN$

3. Action of 3-chloromethylisoxazole on tri-n-propyl phosphite. 5.2 g tri-n-propyl phosphite and 3 g 3-chloromethylisoxazole were heated in a small distillation flask in an oil bath. n-Propyl chloride (b.p. 46.5°) started to come off at about 160°. Heating was continued for an hour. Distillation in vacuum gave about 4 g (65.5%) of viscous, colorless liquid boiling at 150-152° (2.5 mm); d_4^{20} 1.1541; n_D^{20} 1.4675; Found MR 59.47; Calculated MR 59.95. The product is soluble in ether, benzene, chloroform and ethanol. The solubility in water is somewhat lower than the solubility of the ethyl ester.

Found %: P 12.42
Calculated %: P 12.54 $C_{12}H_{24}O_4PN$

4. Action of 3-chloromethyl soxazole on sodium diethyl phosphite. To an ethereal solution of sodium diethyl phosphite, prepared from 0.9 g Na and 6.21 g $(C_2H_5O)_2POH$ (the theoretical amount is 5.21 g), was added 4.33 g 3-chloromethyl soxazole. The solution was refluxed for 6 hours. Separation of the precipitated sodium chloride, which came down in a colloidal form, was facilitated by addition of a small amount of water. After filtration, the ethereal solution was dried with calcium chloride and distilled in vacuum. Yield 1.4 g (17%) product with b.p. 148° (5 mm); n_D^{20} 1.4625.

Hydrolysis of reaction products. 0.5 g ethyl ...oxazolylmethanephosphonate was heated with dilute hydrochloric acid at 120-125° for 5 hours. Evaporation on the water bath with repeated addition of water yielded a dark resinous residue which did not crystallize after prolonged standing in a desiccator over sulfuric acid. Hydrolysis of the n-propyl ester with hydrochloric acid gave a similar result. No pure product of hydrolysis was isolated.

Alkaline hydrolysis. 1.9 g ethyl ester was heated to boiling with 4 g NaOH in 50 ml water for 4.5 hours. The solution was neutralized with hydrochloric acid and evaporated to dryness. The residue was extracted with absolute ethanol. Evaporation of the alcohol left a non-crystallizing, viscous liquid. This was dissolved in water and boiled with barium carbonate. The solution of barium salt was digested with animal charcoal and evaporated to dryness on a water bath. The dried, slightly yellowish residue was analyzed for barium.

Found %: Ba 47.08
Calculated %: Ba 46.03. $C_4H_6C_6NPBa$

5. Action of 3-chloromethylisoxazole on tri-n-butyl phosphite. 3.9 g 3-chloromethylisoxazole and 8.4 g tributyl phosphite (1 mole to 1 mole ester) were heated in an Arbuzov flask. Reaction commenced at 170° (temperature of the mixture). The mixture was heated at 170-180° for 2 hours and at 180-195° for 1 hour. 2 g n-butyl chloride was separated (b.p. 77-79°; n_D^{20} 1.4065). Distillation of the reaction products gave a substance with b.p. 155-156° (1 mm); 3.4 g (35.5% of the theoretical); d_4^{20} 1.0750; n_D^{20} 1.4575; Found MR 69.77; calculated MR 69.19.

6. Reaction of 2,3-di(ω-bromomethyl)-quinoxaline with trimethyl phosphite. 2,3-di(ω-bromomethyl)-quinoxaline was prepared by condensation of dibromodiacetyl with o-phenylenediamine in ethanolic solution [5]. After crystallization from ethanol with use of active carbon, the m.p. was 151-152° (literature 150°). 2 g 2,3-di-(ω-bromomethyl)-quinoxaline and 1.65 g trimethyl phosphite in 10 ml dry benzene were boiled for 1.5 hours. After driving off the greater part of the benzene, the reaction products were further heated at 130° for 5 min. After cooling, the liquid product was poured on to a watch glass. Addition of n-heptane and rubbing with a glass rod caused crystallization. Yield 1.7 g (70.8%) crystals with a wide melting point. Three crystallizations from ether gave prisms melting at 115-116° to a yellow liquid. The prisms are soluble in benzene, ether, methanol and ethanol, also in water.

Found %: P 16.43
Calculated %: P 16.57 $C_{16}H_{20}O_6P_2N_2$.

Hydrolysis of the ester. 0.64 g ester was heated in a sealed tube with 15 ml dilute (1:1)hydrochloric acid at 100° for 7 hours. The contents of the tube were evaporated in a small beaker on a water bath with repeated additions of water until the hydrochloric acid had been completely removed. The product was purified by recrystallization from water with addition of active carbon. Light-yellow crystals; they darkened when heated above 200° and melted at about 234° with decomposition into a dark liquid.

Found %: P 19.06
Calculated %: P 19.49 $C_{16}H_{12}O_6P_2N_2$.

7. Reaction of 2,3-di(ω-bromomethyl)-quinoxaline with triethyl phosphite. 1.5 g 2,3-di(ω-bromomethyl)-quinoxaline and 1.67 g triethyl phosphite were heated in 10 ml dry benzene for 5 hours. After part of the benzene had been driven off, 3-4 ml n-heptane was added to the flask. A white precipitate immediately came down—1 g (50 %). This was recrystallized from n-heptane, m.p. 92-93°. Its properties resembled those of the preceding product.

Found %: P 14.47
Calculated %: P 14.41 $C_{18}H_{28}O_6P_2N_2$.

Hydrolysis of the ethyl ester. Hydrolysis of the product was effected as before by heating with dilute hydrochloric acid in a sealed tube at 110-115° for 5 hours. An acid was obtained which darkened when heated to 210° and melted to a dark liquid on further heating.

8. Reaction of 2,3-di(ω-bromomethyl)-quinoxaline with triisopropyl phosphite. A mixture of 1.5 g of the dibromide and 2.08 g phosphite in 10 ml dry benzene was heated to the boil in an Arbuzov flask for 2 hours. The benzene was then driven off and the residue heated for 5 min. at 140°. Addition of n-heptane brought down crystals in the form of colorless needles; yield 1.2 g (51.8%). After recrystallization from n-heptane the product melted at 102-103°, readily soluble in benzene, ether, ethanol, and methanol; soluble in water.

Found %: P 12.83
Calculated %: P 12.75 $C_{22}H_{36}N_2P_2O_6$.

9. Reaction of 2,3-di(ω-bromomethyl)-quinoxaline with tri-n-propyl phosphite. 1.5 g 2,3-di(ω-bromomethyl)-quinoxaline and 2.08 g tri-n-propyl phosphite were heated in 10 ml dry benzene for 3 hours. After working up in the usual way, the product did not crystallize. After long standing in a small open beaker, the product remained in the form of a thick liquid, soluble in organic solvents and water.

10. Reaction of 2,3-di(ω-bromomethyl)-quinoxaline with sodium dimethyl phosphite.

Experiment 1. An ethereal solution of 2,3-di(ω-bromomethyl)-quinoxaline and sodium dimethyl phosphite (1 mole of quinoxaline to 2 moles of sodium salt) was refluxed on a water bath for 3 hours. The quinoxaline derivative was recovered unchanged.

Experiment 2. A similar experiment was carried out in ligroine solution (b.p. 80-110°). After the precipitated sodium chloride had been filtered off and the ligroine distilled off from the filtrate, the reaction product did not crystallize and remained in the form of a viscous, non-crystallizing liquid with a brown color. Hydrolysis of this liquid with dilute hydrochloric acid led to resinification.

11. Reaction of quinoxaline with diethylphosphorous acid. Quinoxaline [6] was prepared by condensation of o-phenylenediamine with the bisulfite compound of glyoxal (m.p. 33-35°). In a small Arbuzov flask were placed 3.6 g diethylphosphorous acid and 1.7 g quinoxaline (2 moles acid to 1 mole quinoxaline). To the resultant solution was added 8-10 drops of an ethanolic solution of sodium ethoxide. The reaction mixture was heated on a water bath, during which process the color changed from light-yellow to a darker shade. After 1.5 hours the

contents of the flask had solidified. 4 g (approx 77 %) crystals was filtered off. After washing with ligroine they melted at 150-150°. Three recrystallizations from benzene with activated carbon gave fine, colorless hairs with m.p. 168-170°; readily soluble in ether, ethanol, chloroform and benzene; soluble in water.

Found %: P 15.75; 15.83

Calculated %: P 15.26. $C_{16}H_{22}N_2P_2O_6$.

Hydrolysis of the product with hydrochloric acid. 0.45 g product was heated in a sealed tube with 15 ml 10% hydrochloric acid at 100°. After a short period the product acquired a dark cherry-red color. Heating was continued for an hour. Evaporation of the products of hydrolysis on a water bath gave a non-crystallizing, reddish-brown mass.

Alkaline hydrolysis. 0.4 g substance was digested with 0.2 g NaOH in 25 ml water for 3 hours. After neutralization, evaporation on a water bath and boiling with active carbon, a resinous product was obtained.

12. Reaction of 2,3-dimethylquinoxaline with dimethyl- and diethylphosphorous acids. 2 g 2,3-dimethylquinoxaline and 3.4 g dimethylphosphorous acid were heated in a small Arbuzov flask with 8 drops of sodium methoxide. At the start the colorless solution became dark cherry-red. On intense cooling with snow and salt the mass did not crystallize; on standing it turned dark-blue and remained thus for a long period. Attempts to distil in vacuum likewise did not give the desired results (the substance decomposed). The reaction product could not be isolated in the pure form. Diethylphosphorous acid did not react at all in these conditions with 2,3-dimethylquinoxaline. After 5 hours' heating of the mixture in a boiling water bath, the starting substances were recovered unchanged.

SUMMARY

1. Reaction of sodium dialkyl phosphite and of trialkyl phosphite with 3-chloromethylisoxazole gave esters of phosphonic acids containing the isoxazole ring.

2. Reaction of trialkyl phosphites with 2,3-di(ω-bromomethyl)-quinoxaline led to the methyl, ethyl and isopropyl esters of 2,3-di(phosphonomethyl)-quinoxaline.

3. The phosphonic ester could not be isolated after reaction of sodium diethyl phosphite with 2,3-di-(ω-bromomethyl)-quinoxaline.

4. Diethylphosphorous acid adds on to quinoxaline under the influence of sodium alcoholate to form 1,4-dihydro-2,3-di(diethylphosphono)-quinoxaline.

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DIPOLE MOMENTS OF SOME DERIVATIVES OF ETHYLPHOSPHONOUS AND ETHYLPHOSPHONIC ACIDS

B. A. Arbuzov and T. G. Shavsha-Tolkacheva

The monoesters of ethylphosphonous acid constitute an interesting group of derivatives of pentavalent phosphorus, which in their structure and the distribution of the dipole moments of the individual bonds are reminiscent of dialkyl esters of phosphorous acid and differ from the latter in that one OR group is replaced by a C_2H_5 group, due to which the monoesters of ethylphosphonous acid only contain one irregular alkoxy group.

We have determined the dipole moments of the following monoesters of ethylphosphonous acid, which were first synthesized by one of us and Rizpolozhensky [1], and we obtained the values of dipole moments set forth in Table 1.

TABLE 1

No.	Formula	Dipole moment in D	No.	Formula	Dipole moment in D
1	$C_2H_5-\underset{\underset{O\quad H}{\|\diagdown\diagup}}{P}-OCH_3$	3.17	7	$C_2H_5-\underset{\underset{O\quad H}{\|\diagdown\diagup}}{P}-OC_6H_{13}$	3.36
2	$C_2H_5-\underset{\underset{O\quad H}{\|\diagdown\diagup}}{P}-OC_2H_5$	3.48	8	$C_2H_5-\underset{\underset{O\quad H}{\|\diagdown\diagup}}{P}-OC_7H_{15}$	3.31
3	$C_2H_5-\underset{\underset{O\quad H}{\|\diagdown\diagup}}{P}-OC_3H_7\text{-}n$	3.37	9	$C_2H_5-\underset{\underset{O\quad H}{\|\diagdown\diagup}}{P}-OC_8H_{17}$	3.27
4	$C_2H_5-\underset{\underset{O\quad H}{\|\diagdown\diagup}}{P}-OC_3H_7\text{-}i$	3.34	10	$C_2H_5-\underset{\underset{O\quad H}{\|\diagdown\diagup}}{P}-OC_9H_{19}$	3.34
5	$C_2H_5-\underset{\underset{O\quad H}{\|\diagdown\diagup}}{P}-OC_4H_9\text{-}n$	3.41	11	$C_2H_5-\underset{\underset{O\quad H}{\|\diagdown\diagup}}{P}-OC_{15}H_{31}$	3.42
6	$C_2H_5-\underset{\underset{O\quad H}{\|\diagdown\diagup}}{P}-OC_4H_9\text{-}i$	3.38			

We see from Table 1 that the dipole moments of monoesters of ethylphosphonous acid vary from 3.17 to 3.48 D and that the mean value for the series is 3.35 D. It is seen that the mean value of the dipole moments of the monoesters of ethylphosphonous acid (3.35 D) is slightly higher than that for the series of dialkylphosphorous acids (2.91 D). The dipole moment of the molecule of a monoester of ethylphosphonous acid is the resultant of the dipole moments of the P=O, P→O, H→P, R→O bonds and of the P→C bond. The molecule of the monoester contains one irregular group which can rotate around the P–O bond.

We have calculated the dipole moments of molecular models of rigid structures and the dipole moment of a molecule with free rotation of the OH group round the P–O bond. Comparison of the dipole moments calculated for the molecular models with the experimentally determined value of the dipole moment shows that the dipole moment of the rigid structure B (Fig. 1) is 1.61 D and differs markedly from the experimentally found magnitude. The dipole moments of models C and A exceed the experimentally found magnitude by 0.2 and 0.1 D, while the dipole moment of the molecule of the monoester with free rotation of the OR group is 3.32 D and nearly exactly corresponds to the experimentally found value of 3.35 D.

Fig. 1.

In the calculation of the dipole moments of rigid models and of a molecule with free rotation of the OR group, we assumed the following values for the valence angles: O = P – O, 118-119°; O–P–C angle equal to O–P–H angle and equal to 100°; we also assumed the following values for the dipole moments of individual bonds: P = O 3,5 D; P ⟶ O 1,2 D; R ⟶ O 1,12 D; H ⟶ P 0,55 D; P ⟶ C 0,8 D [2].

We calculated the interatomic distances of models of the molecule of monoester with allowance for the radius of the spheres of action of the van der Waals forces and we reached the conclusion that free rotation of the OR groups round the PO bond is possible in the molecule of the monoester since during rotation the spheres of action of the van der Waals forces of the methyl and methylene groups are not superimposed. The interatomic distance of the P–O bond is equal to 1,76 A; that of the R–O bond 1,43 A; that of the P–H bond 1,47 A; and that of the P–C bond 1,87 A. Consequently for monoesters of ethylphosphonous acid we can propose a pyramidal structure with a O = P–O angle of 118°, and an O–P–C angle equal to the O–P–H angle and equal to 100°, with free rotation of the OR group round the P–O bond; the dipole moment of the P–C bond is 0,8 D and is directed from the phosphorus to the carbon.

The direction of the dipole moment of the P–C_2H_5 bond from phosphorous to carbon is retained in esters of ethylphosphonous acid, the structure and arrangement of the dipole moments of the individual bonds of which are reminiscent of those in esters of thiophosphoric acid and they differ from the latter in that one alkoxy group is replaced by an ethyl group. esters of ethylthiophosphonic acid contain only two irregular alkoxy groups which are able to rotate round the P–O bond.

A study of $P_4O_6S_4$ by the electron diffraction method gave a value of 101,5° ± 1° for the O–P–O angle, and a value of 116,5° [3] for the O–P = S angle. On the basis of these results for esters of thiophosphoric acid a pyramidal structure was proposed with a S = P–O angle of 118-119°, and a O–P–O angle of 100°. For esters of ethylphosphonic acid we also assume a pyramidal structure with a O–P–O angle equal to the O–P–C angle and equal to 100°; also a S–P–O angle equal to 118-119°, since substitution of an alkoxy group by ethyl does not introduce great difference in the geometrical structure of the molecule and cannot seriously influence the magnitude and direction of the dipole moments of the individual bonds.

We only had two esters of ethylthiophosphonic acid available for measurement: the ethyl and n-propyl esters prepared by one of us and Rizpolozhensky [4]. The dipole moments of the esters of ethylthiophosphonic acid are set forth in Table 2.

TABLE 2

No.	Formula	Dipole moment in D
1	$(C_2H_5O)_2-\underset{\underset{S}{\|}}{P}-C_2H_5$	3,22
2	$(C_3H_7O)_2-\underset{\underset{S}{\|}}{P}-C_2H_5$-n	2,95

The dipole moment of the n-propyl ester is a little lower, probably due to inadequate purity of the sample, as reflected in the molecular refraction: found MR 57,80; calculated MR 57,08.

We calculated the dipole moments of molecular models of rigid structure and with allowance for rotation of the OR group round the P–O bond. On the basis of a comparison of the experimentally found values of the dipole moments with those calculated for various molecular models, it can be concluded that the dipole moments of the rigid models are 4,20 D for model A_1, 0,77 D for model B_1 and 2,42 D for model C_1 (Fig. 2.), these differ considerably from the values found. The dipole moment of a molecule calculated on the assumption of possible free rotation of two OR groups round the P = O bonds is equal to 2,98 D and comes nearest to the experimentally determined value. The following values of the dipole moments of the individual bonds were used in the calculation of the dipole moments of molecular models: P = S 3,6 D; P ⟶ O 1,2 D; R ⟶ O 1,12 D [5]. The dipole moment of the P ⟶ C bond was taken as 0,8 D, and the direction from phosphorus to carbon.

For the explanation of the possibility of free rotation of the two OR groups round P–O bonds we considered the interatomic distances of the individual models with free rotation, allowing for the radius of action of the van der Waals forces of the methyl and methylene groups. For the esters of ethylthiophosphonic acid, model A_1 has

the least overlapping of the spheres of action of the van der Waals forces of the methyl groups and therefore this model is highly improbable for esters of ethylthiophosphonic acid. Models B_1 and C_1 are possible for esters of ethylthiophosphonic acid since they do not have overlapping of the spheres of action of the van der Waals forces, and hence esters of ethylthiophosphonic acid can only execute an oscillatory movement with an amplitude of 180° at which model C_1 passes into model B_1 and again into C_1. The dipole moment of the molecular model of the ester of ethylthiophosphonic acid calculated for synchronous oscillation of two OR groups round the P–O bond, when the OR groups successively occupy the positions indicated in models C_1 and B_1 and again in C_1, is equal to 1.86 D and differs by 1.00 D from the experimentally found value.

This considerable difference between the experimental and the calculated dipole moment, when assuming paired synchronous oscillation of two OR groups round the P–O bond, suggested to us the possibility of molecular models of esters of ethylthiophosphonic acid in which both OR groups rotate round the P–O bonds synchronously, but during the movement they occupy a different position in respect to the plane of the P = O bond.

The following four models (Fig. 3.) may be advanced for esters of ethylthiophosphonic acid: A_2, B_2, C_2, D_2.

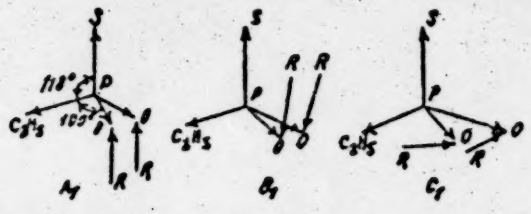


Fig. 2

The dipole moment of model A_2 proved to be 1.57 D, that of model B_2 3.27 D, that of C_2 3.53 D and that of D_2 4.74 D. The dipole moment of a molecule of ester of ethylthiophosphonic acid, calculated on the above assumption of synchronous rotation of the OR groups round the P–O bond, as a mean arithmetic μ of models A_2, B_2, C_2, and D_2 is equal to 2.53 D and differs by 0.4 D from the experimental value.

On the basis of the above considerations it may be suggested that completely free rotation is impossible in esters of ethylthiophosphonic acid, but that there is a possibility of synchronous rotation around the P–O bond to the extent of 360°, as represented for the series of models A_2, B_2, C_2, D_2.

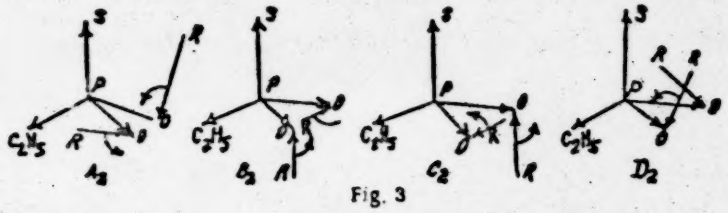


Fig. 3

Continuing our studies of the dipole moments of organophosphorus compounds, it seemed of interest to us to measure the dipole moments of esters of trichloromethylethylphosphonic acid in order to determine the magnitude and direction of the dipole moment of the $P-C_2H_5$ bond in esters of trichloromethylethylphosphonic acid. In respect of their structure and the distribution of dipole moments of the individual bonds, the esters of trichloromethylethylphosphonic acid resemble the esters of monoalkylphosphonic acid, only differing from the latter by the fact that one OR group in the esters of monoalkylphosphonic acids is substituted by the trichloromethyl radical CCl_3.

For esters of monoalkylphosphonic acids we assumed a pyramidal model with a O=P–O angle of 118-119° and a O=P–C angle of 100°, since the electron diffraction data in the literature indicate that the O–P–O angle is equal to the O–P–C angle and each is equal to 100° [2]. For esters of trichloromethylethylphosphonic acid we likewise assumed a pyramidal structure with O–P=O angles equal to 118° and O–P–C angles equal to 100°.

The resultant moment of the molecule of an ester of trichloromethylethylphosphonic acid is made up from the dipole moments of the P = O bond, the P ⟶ O bond, the R ⟶ O bond, the $P-C_2H_5$ bond and the $P-CCl_3$ bond. The dipole moment of the P = O bond is assumed to be 3.5 D, that of the P–O bond 1.2 D, that of the R–O bond 1.12 D. By analogy with esters of monoalkylphosphonic acids, the dipole moment of the $P-C_2H_5$ bond is assumed to be 0.8 D and its direction from phosphorus to carbon. The dipole moment of the $P-CCl_3$ bond is compounded from the dipole moment of the P–C bond and the moment of the $C-Cl_3$ bond. We assume a value of 0.8 D for the moment of the P – C bond, and we assume the moment of the $C-Cl_3$ bond to be equal to that of the C – Cl bond, i.e., 1.5 D. Since both the dipole moments lie on one straight line, the dipole moment of the $P-C-Cl_3$ bond is equal to 2.3 D.

We measured the dipole moments of three esters of trichloromethylethylphosphonic acid: the methyl, ethyl and propyl esters, and obtained the results set forth in Table 3. The esters of trichloromethylethylphosphonic acid were likewise synthesized by Razpolozhensky and kindly placed at our disposal [4].

TABLE 3

No.	Formula	Dipole moment in D
1	$C_2H_5-P(=O)(-OCH_3)-CCl_3$	3.20
2	$C_2H_5-P(=O)(-OC_2H_5)-CCl_3$	3.15
3	$C_2H_5-P(=O)(-OC_3H_7\text{-}n)-CCl_3$	3.29
4	$(C_2H_5O)_2-P(=O)-CCl_3$	3.25

As we see from Table 3, the dipole moments of esters of trichloromethylethylphosphonic acid range from 3.15 to 3.29 D and the mean value for the series is 3.21 D.

We calculated the D of molecular models of rigid structures and of models allowing for free rotation of OR groups, assuming the dipole moment of the P – C bond to be 0.8 D, and that of the P–CCl_3 bond to be 2.3 D and the direction from phosphorus to chlorine. The dipole moment of the rigid structure A_3 is equal to 3.51 D; that of B_3 is equal to 2.71 D, and differs from the experimentally found value, while the dipole moment of the model with free rotation of the OR groups is 2.33 D.

If the direction of the dipole moment of the P–C–Cl_3 bond in the molecule of an ester of trichloromethylethylphosphonic acid is assumed to be from phosphorus to carbon and chlorine, and the dipole moment of the P – C bond is taken to be equal to 0.8 D, then the dipole moment of the structure A_3 is equal to 3.56 D and that of B_3 is equal to 1.97 D. The dipole moment on the assumption of free rotation of OR groups becomes equal to 3.27 D and nearly equal to the experimentally determined value (Fig. 4). Consequently, if we assume for an ester of trichloromethylethylphosphonic acid a dipole moment of the P–C–Cl_3 bond, direction from phosphorus to carbon and chlorine, of 2.3 D, then the experimentally determined dipole moment (3.21 D) approaches most closely to that calculated on the assumption of a dipole moment of 0.8 D for the P–C bond and a direction from carbon to phosphorus (3.27 D). However, a direction of the dipole moment of the P–C_2H_5 bond from carbon to phosphorus is at variance with the general course of shift of electrons in the molecule of an ester of trichloromethylethylphosphonic acid.

On the other hand, the dipole moment of the trichloromethyl radical may be calculated from the dipole moment of chloroform, which is 1.15 D. The dipole moment of CCl_3 is then equal to 0.75 D with a direction from carbon to chlorine, while the dipole moment of the P–C–Cl_3 bond is equal to the sum of the dipole moments of the P–C and C–Cl_3 bonds and is equal to 1.6 D if the dipole moment of the P–C bond is directed from phosphorus to carbon, and nearly equal to zero if the dipole moment of the P–C bond is directed from carbon to phosphorus.

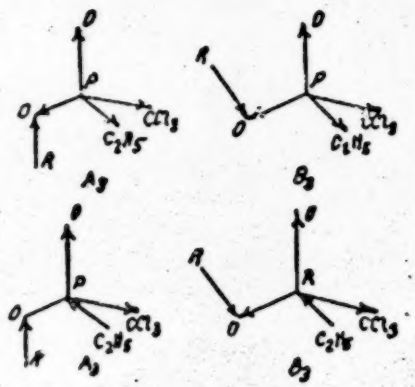


Fig. 4

For determination of the magnitude and direction of the dipole moment of the P–C–Cl_3 bond we made use of the dipole moment of diethyl trichloromethylphosphonate. The structure of the molecule of diethyl trichloromethylphosphonate is similar to that of esters of phosphoric acid, only differing in that one OR group is replaced by the trichloromethyl radical, CCl_3. The dipole moment of diethyl trichloromethylphosphonate was measured by us and found to be 3.25 D.

If we assume that the dipole moment of the $P-CCl_3$ bond is 1.60 D and is directed from phosphorus to carbon and chlorine, then the dipole moment of the molecule of an ester of trichloromethylphosphonic acid with free rotation of the OR groups is 2.55 D, which is less by 0.7 than the experimentally determined value. The experimental value of the dipole moment of diethyl trichloromethylphosphonate (3.25 D) corresponds to that calculated on the assumption of free rotation of the OR groups only in the event that the dipole moment of the $P-CCl_3$ bond is equal to zero or 4.15 D.

A zero value of the dipole moment of the $P-CCl_3$ bond could only arise if the dipole moment of the P–C bond was equal to 0.8 D and directed from carbon to phosphorus, and if the dipole moment of the $C-Cl_3$ bond was 0.8 D and directed from carbon to chlorine. The change of the electronegativity of the P–C bond from 2.1 to 2.5 D and of the C–Cl bond from 2.5 to 3.0 D is nearly identical, and notwithstanding the considerable electron shift, in the P = O bond and in the two P–O bonds, the phosphorus atom is more electronegative than the C atom due to the intense electronic shift in the three C–Cl bonds.

If we assume that the dipole moment of the $P \leftarrow C \rightarrow Cl_3$ bond is also zero in the molecule of ester of trichloromethylethylphosphonic acid, then the dipole moment determined by experiment (3.21 D) nearly coincides with the value (3.05 D) calculated on the assumption of a pyramidal structure for the molecule of ester of trichloromethylethylphosphonic acid. The dipole moment of the $P-C_2H_5$ bond is assumed to be equal to 0.8 D and directed from phosphorus to carbon, while the irregular alkoxy group may be able to rotate freely round the P–O bond.

Consideration of the interatomic distances of the molecule of ester of trichloromethylethylphosphonic acid indicates the possibility of free rotation of the OR groups.

EXPERIMENTAL

The dielectric constants and densities of monoesters of ethylphosphonous acid, of esters of ethylphosphonic acid and of esters of trichloromethylphosphonic acid were determined in benzene solutions at 25°. The dipole moments were calculated from the formula:

$$\mu = 0.0127 \cdot 10^{-18} \sqrt{(P_{\infty} - P_{el.} - P_{at.}) \cdot 298},$$

where $P_{el.}$ is the MR and is calculated from the Lorentz-Lorenz formula; P_{at} is equal to 5% of P_{el}. The compounds had the constants set forth in the paper of Arbuzov and Rizpolozhensky [2,4]. The determined values of dielectric constants, densities and polarizations of the benzene solutions of various concentrations of the investigated substances are set forth in Tables 4 to 20.

TABLE 4

$C_2H_5-P(=O)(H)-OCH_3$

c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.004159	2.3339	0.8749	27.51	244.2
0.008762	2.3982	0.8764	28.63	232.1
0.01260	2.4533	0.8765	29.22	233.6
0.01554	2.4917	0.8782	29.72	226.0
0.01932	2.5575	0.8786	30.61	233.4
0.02192	2.6020	0.8798	31.17	234.4
0.00000	2.2725	0.8742	26.61	

$P_{\infty} = 235.00$ $P_{A+E} = 26.80$

$P_{or} = 208.20$; $\mu = 3.17$ D

TABLE 5

$C_2H_5-P(=O)(H)-OC_2H_5$

c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.002004	2.3017	0.8740	27.16	283.7
0.002911	2.3219	0.8743	27.39	276.5
0.004279	2.3456	0.8746	27.72	278.3
0.005486	2.3628	0.8750	27.97	268.0
0.007205	2.3888	0.8752	28.36	264.5
0.008784	2.4125	0.8754	28.70	270.1

$P_{\infty} = 285.0$; $P_{A+E} = 32.15$

$P_{or} = 252.85$ $\mu = 3.48$ D

TABLE 6

$C_2H_5-\underset{\underset{O}{\|}}{\overset{H}{\underset{|}{P}}}-OC_3H_7\text{-}n$

c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,003298	2,3217	0,8741	27,39	255,4
0,003801	2,3334	0,8739	27,59	260,9
0,006106	2,3629	0,8749	28,02	251,5
0,008510	2,4033	0,8756	28,30	257,6
0,010150	2,4130	0,8754	28,78	237,8

P_{∞} = 274,00; P_{el} = 37,15

P_{or} = 236,85 μ = 3,37 D

TABLE 7

$C_2H_5-\underset{\underset{O}{\|}}{\overset{H}{\underset{|}{P}}}-OC_3H_7\text{-}i$

c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,002039	2,3032	0,8740	27,10	251,7
0,004723	2,3478	0,8742	27,80	270,7
0,002748	2,3158	0,8739	27,30	267,1
0,005482	2,3586	0,8749	27,94	263,0
0,006085	2,3684	0,8747	28,10	265,8
0,007248	2,3846	0,8750	28,35	261,6

P_{∞} = 270,0; P_{el} = 37,10;

P_{or} = 232,90; μ = 3,34 D

TABLE 8

$C_2H_5-\underset{\underset{O}{\|}}{\overset{H}{\underset{|}{P}}}-OC_4H_9\text{-}n$

c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,001572	2,2999	0,8743	27,04	283,1
0,004244	2,3423	0,8745	27,71	279,7
0,002762	2,3178	0,8744	27,34	277,6
0,005079	2,3548	0,8742	27,93	279,6
0,007410	2,3934	0,8749	28,52	278,3
0,006648	2,3840	0,8749	28,36	281,7
0,000	2,2725	0,8734	26,64	

P_{∞} = 284,0 P_{A+E} = 41,97; P_{op} =242,00; μ=3,41 D

TABLE 9

$C_2H_5-\underset{\underset{O}{\|}}{\overset{H}{\underset{|}{P}}}-OC_4H_9\text{-}i$

c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,002289	2,3051	0,8743	27,15	243,2
0,00300	2,3169	0,8738	27,34	259,1
0,004785	2,3436	0,8745	27,75	258,2
0,005716	2,3559	0,8746	27,95	255,4
0,006073	2,3615	0,8747	28,01	252,1
0,008246	2,3821	0,8755	28,36	235,1

P_{∞} = 280,00; P_{A+E} = 42,00

P_{or} = 238,00; μ = 3,38 D

TABLE 10

$C_2H_5-\underset{\underset{O}{\|}}{\overset{H}{\underset{|}{P}}}-OC_5H_{11}$

c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,002581	2,3147	0,8741	27,33	289,1
0,001408	2,2945	0,8736	26,95	282,9
0,002995	2,3215	0,8738	27,44	294,4
0,003828	2,3340	0,8737	27,65	290,1
0,005003	2,3550	0,8743	27,99	295,7
0,006636	2,3822	0,8746	28,41	292,2
0,0000	2,2725	0,8734	26,64	

P_{∞} = 286,0. P_{A+E} = 51,74; P_{op} =234,26. μ = 3,36 D

TABLE 11

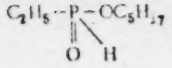
$C_2H_5-\underset{\underset{O}{\|}}{\overset{H}{\underset{|}{P}}}-OC_7H_{15}$

c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0,001721	2,2986	0,8738	27,07	277,9
0,003648	2,3301	0,8738	27,61	290,4
0,002285	2,3060	0,8738	27,19	266,8
0,004120	2,3365	0,8738	27,72	286,6
0,004665	2,3454	0,8739	27,86	286,7
0,006193	2,3696	0,8739	28,27	290,0

P_{∞} = 284,0. P_{A+E} = 56,72

P_{or} = 227,28 μ = 3,33 D

TABLE 12

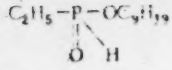


c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.001289	2.2938	0.8739	26.99	284.0
0.002151	2.3076	0.8739	27.23	310.0
0.002838	2.3149	0.8739	27.24	287.9
0.003944	2.3324	0.8739	27.59	280.6
0.004650	2.3435	0.8744	27.84	289.1
0.005333	2.3528	0.8744	27.99	284.9

P_{∞} = 284.00; P_{A+E} = 61.62.

P_{or} = 222.38 μ = 3.27 D

TABLE 13

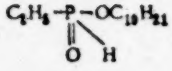


c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.002737	2.3093	0.8734	27.29	303.5
0.001477	2.2955	0.8734	27.06	299.0
0.003587	2.3272	0.8734	27.62	295.3
0.004568	2.3417	0.8734	27.87	294.8
0.006518	2.3429	0.8734	28.44	300.4
0.005252	2.3568	0.8734	28.12	308.1
0.0000	2.2725	0.8734	26.64	

P_{∞} = 299.0; P_{A+E} = 65.49.

P_{or} = 232.51; μ = 3.34 D

TABLE 14

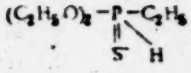


c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.002243	2.3077	0.8736	27.17	302.5
0.001192	2.2921	0.8735	26.98	312.1
0.003384	2.3253	0.8735	27.58	305.3
0.003902	2.3308	0.8735	27.70	296.2
0.004411	2.3401	0.8735	27.85	305.7
0.005152	2.3570	0.8735	28.14	316.7

P_{∞} = 315.00; P_{A+E} = 70.00

P_{or} = 243.00; μ = 3.42 D

TABLE 15

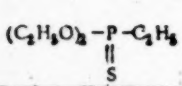


c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.002147	2.3099	0.8740	27.24	264.1
0.004343	2.3372	0.8740	27.71	272.9
0.006183	2.3611	0.8750	28.09	260.5
0.007095	2.3769	0.8750	28.35	266.8
0.008473	2.3992	0.8761	28.66	265.9
0.0000	2.2725	0.8732	26.64	

P_{∞} = 273.00; P_{A+E} = 50.00

P_{or} = 223.00; μ = 3.27 D

TABLE 16

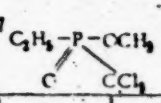


c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.001829	2.2938	0.8738	27.04	233.7
0.003598	2.3156	0.8743	27.39	233.5
0.004333	2.3248	0.8740	27.58	241.6
0.005933	2.3461	0.8748	27.95	243.9
0.007539	2.3668	0.8752	28.28	242.6
0.0000	2.2725	0.8732	26.65	

P_{∞} = 242.00 P_{A+E} = 60.69

P_{or} = 181.31 μ = 2.95 D

TABLE 17



c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.002836	2.3121	0.8757	27.31	257.5
0.001297	2.2910	0.8741	26.95	263.0
0.004144	2.3298	0.8770	27.58	250.3
0.005779	2.3543	0.8790	27.95	250.2
0.007616	2.3798	0.8803	28.36	251.8
0.0000	2.2725	0.8731	26.64	

P_{∞} = 261.0; P_{A+E} = 48.22;

P_{or} = 212.78 μ = 3.20 D

TABLE 18

$C_2H_5-P(O)(CCl_3)-OC_2H_5$

c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.003484	2.3241	0.8763	27.50	262.9
0.001403	2.2929	0.8744	26.96	259.6
0.004775	2.3422	0.8773	27.70	247.7
0.005585	2.3588	0.8787	27.98	255.4
0.006608	2.3694	0.8790	28.22	266.5
0.0000	2.2725	0.8732	26.64	

P_∞ = 260.0; P_{A+E} = 53.41;

P_{or} = 206.59; μ = 3.15 D

TABLE 19

$C_2H_5-P(O)(CCl_3)-OC_3H_7\text{-}n$

c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.001593	2.2966	0.8745	27.07	282.9
0.002839	2.3168	0.8753	27.40	290.6
0.003958	2.3309	0.8769	27.62	271.3
0.004939	2.3490	0.8775	27.91	283.2
0.007142	2.3842	0.8796	28.48	284.0

P_∞ = 283; P_{A+E} = 57.78

P_{op} = 225.22, μ = 3.29 D

TABLE 20

$(C_2H_5O)_2-P(O)-CCl_3$

Mol. Wt. 255.5. Found MR 50; calculated MR 50.25

c_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.001463	2.2931	0.8755	26.97	272.8
0.002965	2.3142	0.8776	27.78	260.5
0.004159	2.3317	0.8785	27.62	270.4
0.005098	2.3465	0.8795	27.83	267.7
0.006071	2.3618	0.8807	28.08	269.2
0.007029	2.3704	0.8814	28.22	257.6
0.0000	2.2725	0.8744	26.64	

P_∞ = 273.0; P_{A+E} = 52.5,

P_{or} = 220.5; μ = 3.25 D

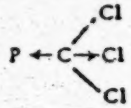
SUMMARY

1. Measurements were made of the dipole moments of the methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, hexyl, heptyl, octyl, nonyl, and decyl esters of ethylphosphorous acid. The mean value of the dipole moment of the series was 3.35 D and it was higher than the mean value for the dialkylphosphorous acids (3.08 D).

2. Measurements were made of the dipole moments of the ethyl and n-propyl esters of ethylthiophosphonic acid (mean value of dipole moment 3.08 D) and of the methyl, ethyl and n-propyl esters of trichloromethylethylphosphonic acid. The mean value for the esters of trichloromethylethylphosphonic acid was 3.21 D.

3. Evaluations were made for all the compounds of the geometrical structure and magnitude and direction of the dipole moments of the individual bonds.

4. Calculations of the dipole moments of esters of trichloromethylethylphosphonic acid for various models lead to the conclusion that the esters have a pyramidal structure with free rotation of the OR groups, with a direction of the dipole moment of the P ⟶ C bond in the ethyl radical from phosphorus to carbon, and a dipole moment of



equal to zero due to compensation of the moments of the P ⟵ C and the C ⟶ Cl_3 bonds.

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[2] T. G. Shavsha, Sci. Memoirs Kazan State Univ., 110, Part 9, 84 (1950).

[3] Hampson, A. J. Stosick, J. Am. Chem. Soc. 60, 1814 (1938).

[4] B. A. Arbuzov and N. I. Rizpolozhensky, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1952, No. 5, 854. (T.p. 765*)

[5] B. A. Arbuzov and T. G. Shavsha, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1951, No. 6, 795.

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*(T.p. = Consultant's Bureau Translation Pagination)

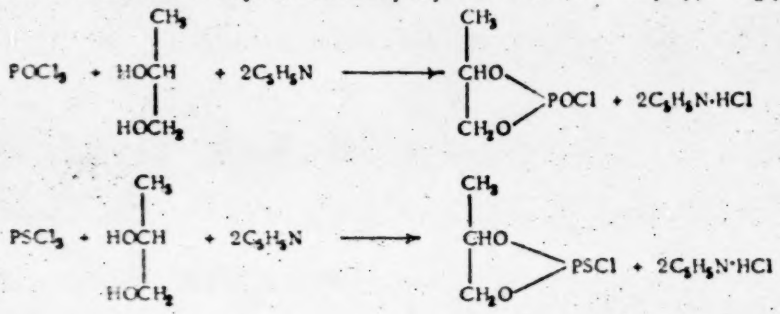
ESTERS OF PROPYLENE GLYCOL PHOSPHORIC AND PROPYLENE GLYCOL THIOPHOSPHORIC ACIDS

B. A. Arbuzov, K. V. Nikonorov and Z. G. Shishova

Cyclic esters of phosphorous acid have recently begun to be studied. Starting in 1945, A. E. Arbuzov and Zoroastrova [1], later in collaboration with Rizpolozhensky [2] and Azanovskaya [3], synthesized and described a series of chlorides and esters of ethylene, propylene, trimethylene and α-chloropropylene glycol phosphorous acids. Esters of glycol phosphoric acids, however, have not previously been studied.

In this communication we present the results of synthesis of cyclic esters of propylene glycol phosphoric and thiophosphoric acids.

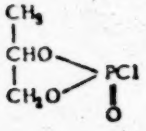
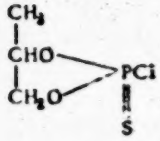
Reaction of phosphorus oxychloride with propylene glycol in presence of hydrogen chloride-binding media yielded the acid chloride of propylene glycol phosphoric acid. Similarly the chloride of propylene glycol thiophosphoric acid was obtained by the action of phosphorus thiochloride on propylene glycol:



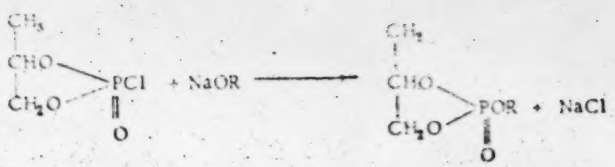
The chlorides of propylene glycol phosphoric and thiophosphoric acids are colorless liquids fuming in the air and resembling the chlorides of dipropylphosphoric and thiophosphoric acids in properties. These compounds are considerably more stable than the corresponding chlorides of phosphorous and thiophosphorous acids. When sealed into glass ampoules they are storable without change for a long period. They react slowly with cold water, but if a base is added to the water they react violently with considerable heat development.

Purification of the chlorides of propylene glycol phosphoric and thiophosphoric acids prepared by the above method was a difficult matter, particularly in respect of the first compound. Vacuum-distillation leads to resinification of a considerable proportion of the crude product and the yield of pure acid chloride is low. Further syntheses of cyclic esters of propylene glycol were effected with the undistilled chlorice of propylene glycol phosphoric acid.

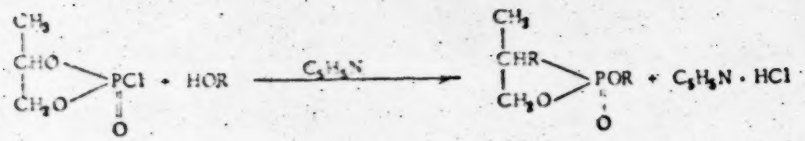
TABLE 1

Formula	B.p. in °C (p in mm mercury)	d_4^{16}	n_D^{16}	Yield in %	MR	
					Found	Calc.
	102-105 (4)	1.4210	1.4520	21	29.31	29.06
	82-84 (3)	1.3902	1.5090	43.5	37.05	37.08

We synthesized the cyclic esters of propylene glycol phosphoric acid by the action of propylene glycol phosphoryl chloride on sodium alkoxides or on alcohols in presence of pyridine according to the following equations:

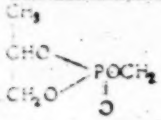
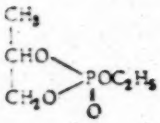
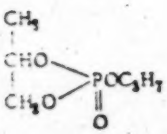
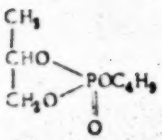
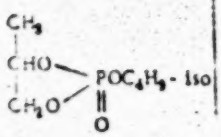


or

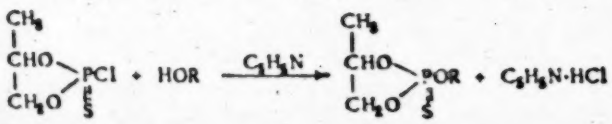


In Table 2 are listed 5 esters prepared by one of the above-mentioned methods. These compounds are colorless or light-yellow liquids with a faint fruity odor, they are perfectly stable to water and, as compounds containing pentavalent phosphorus, their reactivity is low.

TABLE 2

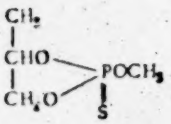
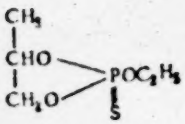
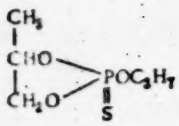
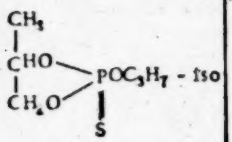
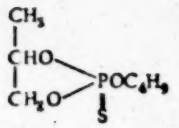
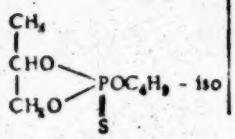
Formula	B.p. in °C (p in mm mercury)	n_D^{20}	d_4^{20}	MR Found	MR Calc.	P, in % Found	P, in % Calc.	Yield %
	114-118 (5)	1.4250	1.2734	30.55	30.47	19.12 19.40	20.4	33
	105-108 (3)	1.4265	1.2095	35.17	35.09	18.59 18.50	18.66	34
	116-118 (3)	1.4290	1.1623	39.98	39.71	17.0 16.6	17.2	34
	127-130 (3)	1.4312	1.1211	44.58	44.64	15.1	15.98	32.2
	122-124 (3)	1.4310	1.1331	44.33	44.64	16.0 16.3	15.98	32.2

In a similar way, by the action of propylene glycol thiophosphoryl chloride on alcohols in presence of pyridine, dimethylaniline or diethylaniline, cyclic esters of propylene glycol thiophosphoric acid were obtained according to the equation:



In Table 3 are set forth the constants of 6 esters prepared by this method. These compounds are colorless, highly refractive liquids with a faint odor. Like the oxygenated analogs, they are stable and extremely inert compounds.

TABLE 3

Formula	B.p. in °C (p in mm mercury column)	n_D^{20}	d_4^{20}	MR		P in %		Yield %
				Found	Calc.	Found	Calc.	
	121-123 (11)	1.4828	1.2639	37.98	37.96	18.45 18.55	18.45	41.8
	107-108 (6)	1.4770	1.2086	42.52	42.58	17.25 16.90	17.03	55
	110-112 (5)	1.4741	1.1696	47.09	47.20	16.10 15.90	15.8	61
	104-106 (3)	1.4750	1.1734	46.50	47.20	15.92 16.14	15.8	38
	114-116 (3)	1.4730	1.1435	15.50	51.81	14.72 15.05	14.78	52.4
	112-115 (3)	1.4720	1.1386	51.65	51.81	14.89 14.88	14.78	38

All the compounds that we have described were tested for insecticidal action on the grain weevil and exhibited an action many times weaker than that of tetraethyl pyrophosphate and tetraethyl monothiophosphate.

EXPERIMENTAL

Preparation of propylene glycol phosphoryl chloride. To a mixture of 22.8 g (0.3 mole) propylene glycol, 89.4 g (0.6 mole) diethylaniline and 200 ml dry ethyl ether was added, with stirring at a temperature (in the reaction flask) of −3.0°, 46.05 g (0.3 mole) phosphorus oxychloride in the course of 2 hours. Cooling was then discontinued and the temperature brought to that of the room. This operation took 2.5-3 hours. The resultant diethylaniline hydrochloride was filtered off; the ether was distilled off from the filtrate and the residue distilled in vacuum to give 10 g (21% of the theoretical) of product with b.p. 102-105 ° (4 mm); d_4^{20} 1.4210; n_D^{25} 1.4520; Found MR 29.31; Calculated for $C_3H_6O_3PCl$ MR 29.06.

Found %: P 29.4; 29.2

Calculated %: P 29.8; $C_3H_6O_2PSCl$

Preparation of propylene glycol thiophosphoryl chloride. Into a three-necked 500 ml flask, equipped with stirrer, dropping funnel and thermometer, were charged phosphorus thiotrichloride, 68 g (0.4 mole), pyridine, 63.5 g (0.8 mole) and 300 ml dry ethyl ether. To the mixture (cooled to −3°) was added 30.5 g (0.4 mole) propylene glycol with continuous stirring over a period of 60 minutes. After the calculated amount of propylene glycol had been added, the reaction mass was gradually heated to 35° and held at this temperature for 2 hours. The pyridine hydrochloride was filtered off (105 g); the ether was driven off and the residue (69 g) distilled in vacuum. Two distillations gave a product with b.p. 82-84° (3 mm) in amount of 30 g or 43.5% of the theoretical; this was a colorless liquid with a pungent, unpleasant odor. d_4^{20} 1.3902; n_D^{20} 1.5090; found MR 37.05 calculated for $C_3H_6O_2PSCl$ MR 37.08.

Found %: P 18.4, 18.2. Cl 20.7, 20.65.

Calculated %: P 18.0 Cl 20.58. $C_3H_6O_2PSCl$.

Preparation of ethyl propylene glycol phosphate. At the start sodium ethoxide was prepared from 3.67 g sodium and 70 ml ethanol in 200 ml dry ethyl ether; 25 g propylene glycol phosphoryl chloride was then added dropwise with stirring and cooling (temperature in flask 0 to 2°). After addition of the calculated amount of acid chloride, stirring was continued for another 2 hours while the temperature was raised to that of the room. The sodium chloride was separated the next day by centrifuging. After the ethanol-ether mixture had been driven off, the residue was fractionated in vacuum. 9 g (24% of the theoretical) of ethyl propylene glycol phosphate was isolated with the following constants: b.p. 105-108° (3 mm); d_4^{20} 1.208; n_D^{20} 1.4265; found MR 35.96; calculated for $C_5H_{11}O_4P$ MR 35.09.

Found %: P, 18.5, 18.59

Calculated: P 18.66. $C_5H_{11}O_4P$.

Ethyl propylene glycol phosphate is a yellow liquid with a pleasant fruity odor.

Preparation of methyl propylene glycol phosphate. The procedure was similar to the previous one. Reactants were 50 ml methanol, 3.67 g metallic sodium, 25 g propylene glycol phosphoryl chloride. Yield 8 g (33% of product with b.p. 114-118° (5 mm) d_4^{20} 1.273; n_D^{20} 1.4250; found MR 30.55; calculated for $C_4H_9O_4P$ MR 30.47.

Found %: P 19.92; 19.40

Calculated %: P 20.4. $C_4H_9O_4P$.

Methyl propylene glycol phosphate is a yellowish liquid with a fairly pleasant odor.

Preparation of propyl propylene glycol phosphate. Reactants were 80 ml propanol, 3.68 g metallic sodium, and 25 g propylene glycol phosphoryl chloride in 150 ml dry ethyl ether. Yield 10 g (34.8%) of product with b.p. 116 - 118° (3 mm). d_4^{20} 1.1623; n_D^{20} 1.4290; found MR 39.93 calculated for $C_6H_{13}O_4P$ MR 39.71.

Found %: P 17, 16.6

Calculated %: P 17.2 $C_6H_{13}O_4P$.

Propyl propylene glycol phosphate is a yellowish liquid with a pleasant odor.

Preparation of butyl propylene glycol phosphate. Reactants were 80 ml butyl alcohol, 3.68 g metallic sodium and 25 g propylene glycol phosphoryl chloride in 100 ml dry ethyl ether. Yield 10 g (32.2% of the theoretical) of product with b.p. 127-130° (3 mm). d_4^{20} 1.1221; n_D^{20} 1.4312; found MR 44.58; calculated for $C_7H_{15}O_4P$ MR 44.64.

Found %: P 15.5

Calculated %: P 15.98. $C_7H_{15}O_4P$.

Butyl propylene glycol phosphate is a yellowish liquid with a pleasant odor.

Preparation of isobutyl propylene glycol phosphate. Reaction conditions were similar to those previously applied. Materials used were 8.5 g isobutanol, 9.08 g pyridine, 100 ml dry ethyl ether, and 18.2 g propylene glycol phosphoryl chloride. Yield 10 g product (32.2% of the theoretical) with b.p. 122-124° (3 mm); d_4^{20} 1.133; n_D^{20} 1.4316; found MR 44.33; calculated for $C_7H_{15}O_4P$. MR 44.64.

Found %: P 16; 16.3

Calculated %: P 15.98. $C_7H_{15}O_4P$.

Isobutyl propylene glycol phosphate is a light-yellow liquid with a fruity odor.

Preparation of methyl propylene glycol thiophosphate. Into a round-bottomed flask, equipped with stirrer, dropping funnel and thermometer, were charged 60 ml dry ethyl ether, 3.2 g (1 mole) methanol and 7.9 g (1 mole) pyridine. The mixture was cooled to +3° and during 15 minutes 17.2 g (1 mole) propylene glycol thiophosphoryl chloride was added at a liquid temperature of +3 to +10°. After the calculated amount of acid chloride had been added, the contents of the flask were stirred at room temperature for 4 hours. The precipitate of pyridine hydrochloride was then filtered off and the ether was taken off through the water jet pump. The residue was washed several times with water, dried with sodium sulfate and distilled in vacuum. The product had b.p. 121-123° (11 mm); yield 7 g (41.8% of the theoretical; d_4^{20} 1.2639; n_D^{20} 1.4828; found MR 37.98; calculated for $C_4H_9O_3PS$ MR 37.96. Methyl propylene glycol thiophosphate is a colorless liquid with an unpleasant odor.

Found %: P 18.45, 18.55
Calculated %: P 18.45 $C_4H_9O_3PS$

Preparation of ethyl propylene glycol thiophosphate. Operating conditions were as above. From 4.6 g (1 mole) ethyl alcohol, 7.9 g pyridine (1 mole), 17.2 g propylene glycol thiophosphoryl chloride in a medium of dry ethyl ether (70 ml) was obtained 10 g product (55% of the theoretical) with b.p. 107-108°; d_4^{20} 1.209; n_D^{20} 1.4770; found MR 42.52; calculated for $C_5H_{11}O_3PS$ MR 42.58. Ethyl propylene glycol thiophosphate is a colorless liquid with an unpleasant odor.

Found %: P 17.25; 16.9
Calculated %: P 17.03. $C_5H_{11}O_3PS$.

Preparation of propyl propylene glycol thiophosphate. Reaction was carried out with 70 ml dry ethyl ether, 6 g (1 mole) propyl alcohol, 7.9 g (1 mole) pyridine, and 17.2 g (1 mole) propylene glycol thiophosphoryl chloride. 12 g product (61% of the theoretical) was obtained with b.p. 110-112° (5 mm); d_4^{20} 1.187; n_D^{20} 1.4741; found MR 47.09; calculated for $C_6H_{13}O_3PS$ MR 47.20

Found %: P 16.1, 15.9
Calculated %: P 15.8 $C_6H_{13}O_3PS$.

The compound is a colorless liquid with an unpleasant odor.

Preparation of isopropyl propylene glycol thiophosphate. From 6 g (1 mole) isopropanol, 7.9 (1 mole) pyridine and 17.25 g propylene glycol thiophosphoryl chloride in 70 ml dry ethyl ether was obtained 6.5 g product with b.p. 104-106° (3 mm); d_4^{20} 1.188; n_D^{20} 1.4740; found MR 46.50; calculated for $C_6H_{13}O_3PS$ MR 47.20. The ester is a colorless liquid with an unpleasant odor.

Found %: P 15.92; 16.14.
Calculated %: P 15.8 $C_6H_{13}O_3PS$.

Preparation of butyl propylene glycol thiophosphate. From 7.4 g (1 mole) butanol, 7.9 g (1 mole) pyridine, and 17.25 g (1 mole) propylene glycol thiophosphoryl chloride in 70 ml dry ether was obtained 11 g product (52.4% of the theoretical) with b.p. 114-116° (3 mm); d_4^{20} 1.1435; n_D^{20} 1.4730; found MR 51.50; calculated for $C_7H_{15}O_3PS$ MR 51.81. Butyl propylene glycol thiophsphate is a colorless liquid with an unpleasant odor.

Found %: P 14.72; 15.05
Calculated %: P 14.78. $C_7H_{15}O_3PS$.

Preparation of isobutyl propylene glycol thiophosphate. From 7.4 g (1 mole) isobutanol, 7.9 g (1 mole) pyridine, and 17.25 g (1 mole) propylene glycol thiophosphoryl chloride in 70 ml dry ethyl ether was obtained 8 g (38% of the theoretical) of product with b.p. 112-115° (3 mm); d_4^{20} 1.138; n_D^{20} 1.4720; Found MR 51.65; Calculated for $C_7H_{15}O_3PS$ MR 51.81. The isobutyl ester is a colorless liquid with an unpleasant odor.

Found %: P 14.89; 14.88
Calculated %: P 14.78 $C_7H_{15}O_3PS$.

SUMMARY

1. A study was made of the action of phosphorus oxychloride and phosphorus thiotrichloride on propylene glycol in presence of hydrogen chloride-binding media. The chlorides of propylene glycol phosphoric and propylene glycol thiophosphoric acids were synthesized.

2. 12 new mixed cyclic esters of phosphoric and thiophosphoric acids were synthesized by the action of pro-

pylene glycol phosphoryl and thiophosphoryl chlorides on sodium alkoxides or on alcohols in presence of pyridine.

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* T.p. = Consultants Bureau Translation pagination.

THE ACTION OF ALKYL HALIDES ON ESTERS OF ANTIMONOUS AND THIOANTIMONOUS ACIDS

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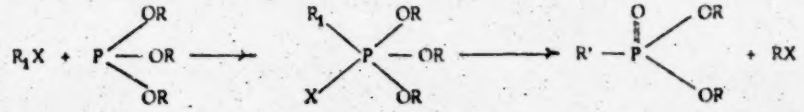
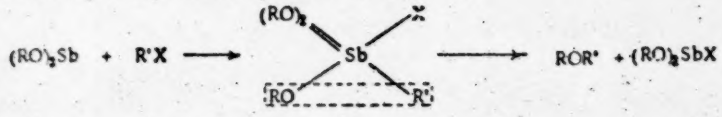
As was shown by A. E. Arbuzov [1], the full esters of phosphorous acid undergo rearrangement under the action of alkyl halides to form esters of alkylphosphonic acids:



Kamai [2] failed to effect the analogous rearrangement of esters of arsenious acid. On acting with alkyl halides upon esters of arsenious acid, he obtained crystalline substances, whose analyses corresponded to products of addition of the alkyl halide to the ester of arsenious acid. Kamai did not investigate these products further.

Experiments on the action of alkyl halides on esters of antimonous acid have not been described. Having engaged in a study of esters of antimonous acid [3], we carried out experiments on the action of alkyl halides on antimonous esters and obtained somewhat unexpected results. The reaction yielded an ether and a dialkoxyhalostibine. The reaction may be represented by the scheme:

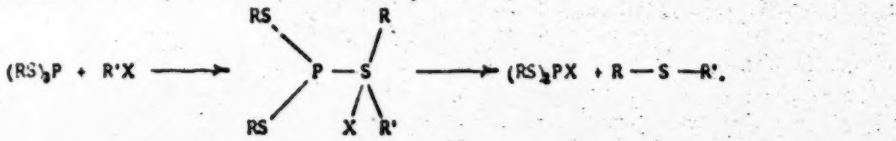


The reaction does not proceed smoothly and is accompanied by the separation of antimony trioxide, metallic antimony, and (in the case of alkyl iodides) iodine. The dialkoxyhalostibines prepared in this way are set forth in the table.

TABLE

$(RO)_2SbX$	M.p. in °C.	B.p. in °C (p in mm mercury)	d_4^{20}	Amount of Sb, in %	
				Found	Calculated
$(C_2H_5O)_2SbI$	72-76	—	—	36.33	35.95
$(C_2H_5O)_2SbBr$	66-67	113-115 (5)	—	42.09	41.73
$(n\text{-}C_4H_9O)_2SbI$		161-163 (10)	1.6481	30.75	30.85
$(n\text{-}C_4H_9O)_2SbBr$		149-150 (6)	1.5931	35.54	35.01
$(i\text{-}C_5H_{11}O)_2SbI$		155-156 (4)	1.6315	28.91	28.79
$(i\text{-}C_5H_{11}O)_2SbBr$		146-148 (5)	1.5559	31.88	32.37

We also synthesized the dialkoxyhalostibines by another route – by the action of acetyl halide on antimonous esters. Kabachnik, Divinsky and Sidorenko [4] showed that in the case of esters of trithiophosphorous acid the action of alkyl halides can proceed differently. The reaction gives chlorides of esters of dithiophosphorous acids, and a thioether is cleaved off. The course of the reaction of Kabachnik and co-workers may be explained by the formation of a sulfonium compound as an intermediate product:



It was interesting to study the reaction of alkyl halides with esters of trithioantimonous acid. Our experiments showed that the reaction of alkyl halides with trithioantimonous esters takes place with considerably greater facility than with antimonous esters, and that it leads to the chloride of the ester of dithioantimonous acid and the

corresponding sulfide:

$$(RS)_3Sb + R'X \longrightarrow (RS)_2SbX + R{-}S{-}R'.$$

The following compounds were prepared in this way:

$(C_2H_5S)_2SbI$ with b.p. 161-162° (7 mm); d_4^{20} 2.2030

$(C_2H_5S)_2SbBr$ with b.p. 151-152° (8 mm); d_4^{20} 2.1099

Splitting-off of an ether by the action of halogenated derivatives on esters of antimonous acid is not limited to simple alkyl halides. Thus, we showed that the action of chloromethylbutyl ether on tributyl antimonite results in extremely facile and smooth splitting-off of formaldehyde dibutylacetal and in the formation of dibutoxychlorostibine, which we previously prepared by the action of acetyl chloride on butyl antimonite [3].

$$(C_4H_9O)_3Sb + ClCH_2OC_4H_9 \longrightarrow (C_4H_9O)_2SbCl + C_4H_9OCH_2OC_4H_9.$$

This reaction may proceed even further. Thus, the action of butylchloromethyl ether on dibutoxychlorostibine brings about ready detachment of dibutylformal and formation of butoxychlorostibine.

$$(C_4H_9O)_2SbCl + ClCH_2OC_4H_9 \longrightarrow (C_4H_9O)SbCl_2 + C_4H_9OCH_2OC_4H_9.$$

Esters of haloacids enter into similar reactions with antimonous esters.

Ethyl bromoacetate reacts with triethyl antimonite to form diethoxybromostibine and ethyl ethoxyacetate:

$$(C_2H_5O)_3Sb + BrCH_2COOC_2H_5 \longrightarrow (C_2H_5O)_2SbBr + C_2H_5OCH_2COOC_2H_5.$$

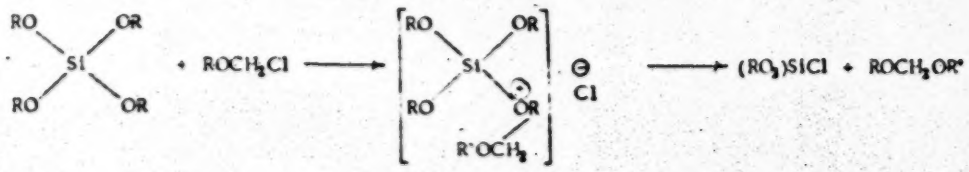
The reaction of esters of antimonous acid with halogenated derivatives may be considered to proceed with intermediate formation of both derivatives of pentavalent antimony

$$(C_2H_5O)_3Sb + RX = [(C_2H_5O)_3\overset{\oplus}{S}bR]\overset{\ominus}{X},$$

and of compounds of the oxonium type:

$$\left[(C_2H_5O)_2Sb-\overset{\oplus}{O}(R)-C_2H_5\right]\overset{\ominus}{X}.$$

It seemed to us that indirect confirmation of the possibility of the reaction proceeding in the second of the above directions might be obtained by experiments on the reaction of α-haloethers on esters of acids other than antimonous acid



Experiment showed, however, that even in very drastic conditions, with prolonged heating at 250-260° of chloromethylmethyl ether with tetraethyl silicate, reaction does not take place. The data obtained speak rather against the oxonium scheme. We must, however, be cautious in drawing a close analogy between orthosilicic esters and esters of antimonous acid. On the other hand, if we accept the scheme for addition of alkyl halide to antimony, the formation of an ether containing a radical of halogenated derivative requires migration of the radical from antimony to oxygen.

All these considerations prompted us to regard the mechanism of the reactions considered in this paper as still unclarified and as requiring further investigations.

EXPERIMENTAL

Preparation of isoamyl antimonite: Into an Arbuzov flask were put 7 g ethyl antimonite and 7.5 g isoamyl alcohol from fusel oil. At 110-120° the ethanol (b.p. 78-84°) came off in amount of 3.6 g. Distillation in vacuum gave a fraction of 7.2 g with b.p. 150.5-151° (3 mm); d_4^{20} 1.189; n_D^{20} 1.4764.

Found %: Sb 31.54
Calculated %: Sb 31.03. $C_{15}H_{33}O_3Sb$.

Action of methyl iodide on ethyl antimonite. 15 g ethyl antimonite and 8.3 g methyl iodide were heated in a sealed tube for 3 hours at 130-135°. After the heating the tube contents consisted of a liquid and a crystalline product, which was filtered. Slight pressure was detected when the tube was opened. The filtrate was fractionated to give 5.1 g substance with b.p. 95-96° (11 mm). This was unreacted ethyl antimonite. The crystalline product had m.p. 72-76°; yield 8.3 g (64.5% of reacted ethyl ester).

Found %: Sb 36.92; 37.08
Calculated %: Sb 35.95 $C_4H_{10}O_3Sb$.

Action of ethyl iodide on ethyl antimonite. 15 g ethyl antimonite and 9.1 g ethyl iodide were heated in a sealed tube for 2.5 hours at 170-180°. The resultant crystalline product was filtered off and washed with ether. Fractionation of the filtrate gave the fractions:

Fr. I., b.p. 33-40°; 2.3 g (ethyl ether).
Fr. II., b.p. 90-92° (7 mm). 6.1 g (ethyl antimonite).

In the tube remained a deposit of metallic antimony, iodine and antimony trioxide.

The crystalline product has m.p. 71-76°, yield 6.4 g (55.6% on the reacted ethyl antimonite.)

Found %: Sb 36.75, 36.33.
Calculated %: Sb 35.95 $C_4H_{10}O_3Sb$.

Action of ethyl bromide on ethyl antimonite. 15 g ethyl antimonite and 6.4 g ethyl bromide were heated in a sealed tube for 4 hours at 190-195°. The crystalline product resulting from the reaction was filtered off and washed with ether. On the walls of the tube was a deposit of antimony, iodine and antimony trioxide. Fractionation gave:

Fr. I., b.p. 34-40°, 2.1 g (ethyl ether)
Fr. II., b.p. 79-81° (3 mm); 2.8 g (ethyl antimonite)
Fr. III., b.p. 109-111° (3 mm), 2.1 g (crystalline product with m.p. 66-67°; yield 4.7 g, 48% of theoretical).

Found %: Sb 42.09; 42.36.
Calculated %: Sb 41.73. $C_4H_{10}O_3BrSb$.

Action of n-propyl bromide on ethyl antimonite. 15 g ethyl antimonite and 7.2 g n-propyl bromide were heated in a sealed tube for 6 hours at 200-205°. The crystalline product resulting from the reaction was filtered and washed with ether. The filtrate was fractionated.

Fr. I., b.p. 60-63°; 2.4 g
Fr. II., b.p. 70-72°; 1.8 g (unreacted propyl bromide)
Fr. III., b.p. 80-82° (3 mm); 4.6 g (ethyl antimonite)
Fr. IV., b.p. 108-111° (3 mm); 2.6 g. M.p. 65-66°

On the walls of the tube was a deposit of antimony trioxide. Fraction I was redistilled and had b.p. 62-63°; n_D^{20} 1.3733; it was ethylpropyl ether. Literature data [6]: b.p. 63.6°; n_D^{20} 1.36948. Yield of crystalline product 3.3 g; 29% of the theoretical. Its physical constants correspond to those of diethoxybromostibine obtained by the action of ethyl bromide on triethoxystibine.

Action of methyl iodide on n-butyl antimonite. 15 g n-butyl antimonite and 6.2 g methyl iodide were heated in a sealed tube for 3.6 hours at 185-190°. Fractionation of the reaction product gave:

Fr. I., b.p. 68-72°, 2.9 g
Fr. II., b.p. 138-160° (8 mm); a few drops
Fr. III., b.p. 161-163° (8 mm); 8.2 g; d_4^{20} 1.6641; yield 54%.

A deposit of antimony, iodine, and antimony trioxide remained on the sides of the tube and flask. Fraction I was redistilled and had b.p. 70-71°; n_D^{20} 1.3793. It was methylbutyl ether. Literature data [7]: b.p. 70.3°;

n_D^{20} 1.3720. Fraction III is a reddish liquid.

Found %: Sb 31.21; 30.75
Calculated %: Sb 30.85 $C_8H_{18}O_2ISb$

Action of ethyl bromide on butyl antimonite. 10.5 g n-butyl antimonite and 3.7 g ethyl bromide were heated for 12 hours at 200-210°. Fractionation gave:

Fr. I., b.p. 90-96°, 2.1 g.
Fr. II., b.p. 149-150° (6 mm); 5.2 g; d_4^{20} 1.5931; yield 49.9%.

On the walls of the tube and flask was a deposit of antimony trioxide. Fraction I was redistilled and had b.p. 92-93°, n_D^{20} 1.3705. It was ethylbutyl ether. Literature data [8]: b.p. 91.4°. Fraction II was a viscous liquid, readily hydrolyzing in the air.

Found %: Sb 35.84; 35.78
Calculated %: Sb 35.01. $C_8H_{18}O_2BrSb$.

Action of methyl iodide on isoamyl antimonite. 8 g isoamyl antimonite and 3 g methyl iodide were heated in a sealed tube for 6 hours at 185-200°. The reaction products were fractionally distilled.

Fr. I., b.p. 87-92°; 1.9 g
Fr. II, b.p. 142-150° (4 mm); a few drops
Fr. III., b.p. 155-156° (4 mm). d_4^{20} 1.6315; 3.8 g; yield 43.2%.

On the walls of the tube and flask was a deposit of iodine, antimony and antimony trioxide. Fraction I was redistilled and had b.p. 90-91°; n_D^{20} 1.3895; it was methylisoamyl ether. Literature data [9]: b.p. 91°. Fraction III was a reddish liquid, easily hydrolyzed in the air.

Found %: Sb. 28.91; 28.61
Calculated %: Sb 28.79 $C_{10}H_{22}O_2ISb$.

Action of ethyl bromide on isoamyl antimonite. 11 g isoamyl antimonite and 5.2 g ethyl bromide were heated in a sealed tube for 9 hours at 185-210°. The reaction products were fractionally distilled:

Fr. I. b.p. 109-112°; 2.8 g
Fr. II., b.p. 146-148° (5 mm). d_4^{20} 1.5559; 4.5 g; yield 42%.

On the walls of the tube and the flask was a deposit of antimony trioxide. Fraction I was redistilled and had b.p. 111-112°; n_D^{20} 1.3923; it was ethylisoamyl ether. Literature data [10]: b.p. 112°. Fraction II was a viscous liquid, easily hydrolyzed in the air.

Found %: Sb 31.88, 31.70
Calculated %: Sb 32.37 $C_{10}H_{22}O_2BrSb$.

Action of hexyl chloride on ethyl antimonite. 7.5 g ethyl antimonite and 3.4 g n-hexyl chloride were heated in a sealed tube for 8 hours at 200-215° and even at 250°. No reaction took place between these compounds.

Action of methyl iodide on ethyl trithioantimonite. 10 g ethyl trithioantimonite and 4.8 g methyl iodide were heated for 2.5 hours at 80-85°. The reaction products were fractionally distilled:

Fr. I., b.p. 67-70°, 2.1 g
Fr. II., b.p. 144-145° (9 mm); 0.6 g
Fr. III., b.p. 162-163° (8 mm), d_4^{20} 2.2030; 3.2 g; yield 26.4 %.

On the walls of the tube and the flask was a depodt of antimony, sulfur and iodine. Fraction I was redistilled and had b.p. 66-68°, n_D^{20} 1.4410; it was methylthioethyl ether. Literature data [11]: b.p. 66.5-67.5°. Fraction III was a reddish liquid with an unpleasant odor, easily hydrolyzed in the air.

Found %: Sb 32.51, 33.14
Calculated %: Sb 32.85 $C_4H_{10}S_2ISb$.

Action of ethyl iodide on ethyl trithioantimonite. 10 g ethyl trithioantimonite and 6.1 g ethyl iodide were heated in a sealed tube at 75-80° for 1.5 hours. The products of reaction were fractionally distilled:

Fr. I., b.p. 90-94°; 3.3 g

Fr. II., b.p. 151-160° (7 mm); 0.6 g
Fr. III., b.p. 161-162° (7 mm); d_4^{20} 2.2028; 5.6 g; yield 46.0%

On the walls of the tube and flask was a deposit of sulfur, iodine and antimony. Fraction I was redistilled and had b.p. 92-93°; n_D^{20} 1.4476; it was ethyl sulfide. Literature data [12]: b.p. 92.2-93°; n_D^{20} 1.4423. Fraction III was the iodoanhydride of ethyl dithioantimonite.

Action of ethyl bromide on ethyl trithioantimonite. 10.5 g ethyl trithioantimonite and 3.9 g ethyl bromide were heated in a sealed tube for 5 hours at 70-75°. The products of reaction were fractionally distilled:

Fr. I., b.p. 90-94°, 2.8 g
Fr. II., b.p. 151-152° (8 mm): d_4^{20} 2.1090; 5.2 g; yield 46.8%.

Fraction I was redistilled and had b.p. 92-93°; n_D^{20} 1.4452; it was diethyl thioether. Fraction II was a yellowish liquid with an unpleasant odor, easily hydrolyzed in the air.

Found %: Sb 38.22; 38.24
Calculated %: Sb 37.61 $C_6H_{10}S_2PrSb$.

Action of chloromethylbutyl ether on butyl antimonite. To 9 g butyl antimonite in an Arbuzov flask was slowly added 3.2 g chloromethylbutyl ether; heat was developed. The reaction products were fractionally distilled:

Fr. I., b.p. 65-70° (11 mm); 3.9 g
Fr. II., b.p. 148-149° (11 mm); d_4^{20} 1.5073; 6.5 g; yield 82%

Fraction I was redistilled and had b.p. 67° (11 mm); d_4^{20} 0.8362; n_D^{20} 1.4075; it was formaldehyde dibutylacetal. Literature data [13]: b.p. 180.5-181°; d_4^{20} 0.8366; n_D^{20} 1.4072. Fraction II was dibutoxychlorostibine. Literature data [3]: b.p. 150-151° (13 mm);

Action of chloromethylbutyl ether on chlorodibutoxystibine. Into a Claisen flask was charged 5.2 g dibutoxychlorostibine, and 2.1 g chloromethylbutyl ether was slowly added; heat was liberated. The whole of the reaction mass crystallized on standing. The reaction products were fractionally distilled:

Fr. I., b.p. 66-69° (11 mm); 2.4 g
Fr. II., b.p. 124-126°; M.p. 84-85°; 3.9 g; yield 86%

Fraction I was redistilled and had b.p. 67° (11 mm); n_D^{20} 1.4076; d_4^{20} 0.8360; it was formaldehyde dibutylacetal. Fraction II was dichlorobutoxystibine. Literature data [3]: b.p. 125-126° (11 mm); M.p. 83-85°.

Action of ethyl bromoacetate on ethyl antimonite. 10 g ethyl antimonite and 6.5 g ethyl bromoacetate were heated in a sealed tube for 12 hours at 160-170°. A crystalline substance came out on standing. The reaction products were subjected to fractionation:

Fr. I., b.p. 50-62° (12 mm)
Fr. II., b.p. 95-98° (12 mm); 2.1 g (ethyl antimonite)
Fr. III., b.p. 125-126° (12 mm); M.p. 67-69°; 6.2 g; yield 66.6%.

Fraction I was redistilled and had b.p. 52-54° (12 mm); d_4^{20} 0.9780; n_D^{20} 1.4092. Literature data [14]: b.p. 158° (752 mm); d_4^{25} 0.9754. Fraction III was bromodiethoxystibine.

Action of chloromethylmethyl ether on ethylorthosilicate. 15 g ethyl orthosilicate and 5.8 g chloromethylmethyl ether were heated in a sealed tube for 36 hours at 250-260°. On fractionation the original substances were recovered unchanged. A part of the chloromethylmethyl ether decomposed.

SUMMARY

1. Alkyl halides react with esters of antimonous acid with cleavage of ethers and formation of dialkoxyhalostibines. In this way the preparation was effected of diethoxy-, dibutoxy-, diisoamyloxybromostibines and of diethoxy-, dibutoxy- and diisoamyloxyiodostibines.

2. Reaction of alkylchloromethyl ethers with antimonous esters leads to separation of the corresponding formals and to formation of alkoxychlorostibines.

$$(RO)_3Sb + CH_2Cl - OR' \longrightarrow (RO)_2SbCl + ROCH_2OR'$$

$$(RO)_2SbCl + CH_2Cl - OR' \longrightarrow (RO)SbCl_2 + ROCH_2OR'$$

3. Alkyl halides readily react with esters of trithioantimonous acid to form dialkyl sulfide and the haloanhydrides of dithioantimonites. The bromoanhydride of diethyl dithioantimonite and the corresponding iodoanhydride were prepared.

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ANOMALOUS REACTIONS OF SODIUM DIETHYL PHOSPHITE AND OF TRIETHYL PHOSPHITE WITH SOME HALOGENATED DERIVATIVES

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In 1929 A. E. Arbuzov and B. A. Arbuzov [1] observed a difference in the course of the reaction of sodium diethyl phosphite with triphenylmethyl chloride and bromide. With triphenylmethyl chloride the normal reaction product is formed – the ester of triphenylmethylphosphoric acid, whereas with triphenylmethyl bromide the free triphenylmethyl radical is formed.

Later we [2] showed that diphenylchloromethane and diphenylbromomethane behave similarly with sodium diethyl phosphite. With the chloride the ester of diphenylmethylphosphonic acid is formed; with the bromide, tetraphenylethane is formed. With a benzyl halide this difference in the behavior of halogen derivatives disappears, and reaction with the chloride, bromide and iodide gives the ester of benzylphosphonic acid. The reactions of dimerization of radicals during the action of sodium diethyl phosphite on halogenated derivatives has also been observed in other cases. A. E. Arbuzov and V. S. Abramov [3] found that in the action of sodium diethyl phosphite on bromoethyl malonate, ethanetetracarboxylic acid ester is formed. Shavan [4] showed that dimerization of radicals proceeds in the reaction of sodium diethyl phosphite with esters of halosubstituted acids.

We studied the reactions of sodium diethyl phosphite and triethyl phosphite with various types of halogen derivatives with the aim of making a close study of the anomalous course of the reaction with sodium diethyl phosphite, and thereby of establishing the causes of this behavior of sodium diethyl phosphite and the halogen derivative during double exchange reactions. As the experiments showed, dinaphthylchloromethane, dinapthylbromomethane, 9-chlorofluorene and 9-bromofluorene do not react with sodium diethyl phosphite even when heated to 140°. Interesting results were obtained with 9,10-dibromophenanthrene and sodium diethyl phosphite in an ethereal medium; phenanthrene was isolated in 90% yield. A similar picture was obtained in the reaction of dibromophenanthrene with triethyl phosphite. Here again phenanthrene was isolated in a yield of over 90%. The phosphorus-containing products of the reaction were not examined in detail. Fractions with constants similar to those of diethylphosphoric acid were isolated.

The following mechanism may be advanced for these reactions: sodium diethyl phosphite and triethyl phosphite function as bromine acceptors; a diradical is formed which is stabilized by formation of phenanthrene.

The reaction of the dibromo compound proceeds in like manner to the reaction of tetramethylethylene dibromide with sodium diethyl phosphite, which leads to tetramethylethylene [2].

Diethyl phosphorous acid could have been formed by hydrolysis of the ester. Formation of diethyl phosphorous acid in the reaction with triethyl phosphite is still unclarified.

We obtained entirely unexpected results on reacting sodium diethyl phosphite or triethyl phosphite with dibenzoylbromomethane and tribenzoylbromomethane. The main products of reaction were respectively dibenzoylmethane and tribenzoylmethane. Distillation of the phosphorus-containing portion of the reaction products in both cases gave a product whose constants and analysis corresponded to diethyl phosphate.

The mechanism of this oxidation-reduction reaction cannot be considered to be clarified. In the present stage of the investigation a radical scheme for the reaction seemed to us most probable:

$$2(C_6H_5CO)_2CHBr + 2NaOP(OC_2H_5)_2 \longrightarrow 2(C_6H_5CO)_2C\overset{H}{\cdots} + 2NaBr + [OP(OC_2H_5)_2]_2.$$

The resultant dibenzoylmethyl radical reacts with the solvent (ether), detaching hydrogen and being reduced to dibenzoylmethane. An alternative route to dibenzoylmethane involves disproportionation of dibenzoylmethyl. In that event, however, tetrabenzoylethylene should be formed, and no trace of the latter could be detected.

Formation of the ethyl phosphate is puzzling. It may be mentioned that when chlorine acts upon sodium diethyl phosphite, the products include triethyl phosphate [5].

Formation of dibenzoylmethane in the reaction with the bromo compound takes place without a solvent. The reaction may be represented by the equation:

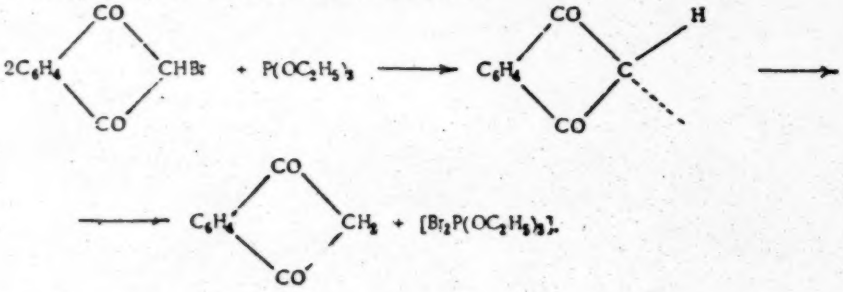
$$2(C_6H_5CO)_2CHBr + P(OC_2H_5)_3 \longrightarrow 2(C_6H_5CO)_2CH\cdots + [BrP(OC_2H_5)_3]$$

In this case the reduction of dibenzoylmethyl must be considered to take place at the expense of the hydrogens of triethyl phosphite. A similar reaction course was observed in the interaction of sodium diethyl phosphite or of triethyl phosphite with tribenzoylbromomethane:

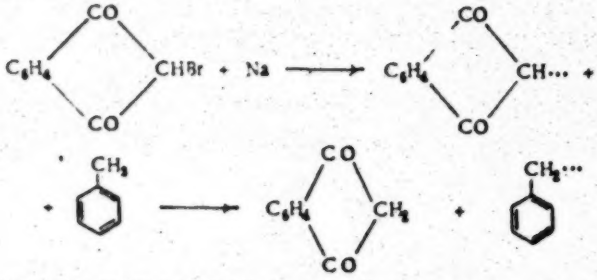
$$(C_6H_5CO)_3CBr + NaOP(OC_2H_5)_2 \longrightarrow (C_6H_5CO)_3C\cdots \longrightarrow (C_6H_5CO)_3CH.$$

In this case again, the reduction must evidently proceed at the expense of the solvent (ether). Triethyl phosphate was isolated in addition to tribenzoylmethane. With the aim of confirming the suggested reaction scheme, we carried out experiments on the action of metallic sodium upon dibenzoylbromomethane and tribenzoylbromomethane in a toluene medium. The reaction does not take place smoothly, although in the first case dibenzoylmethane and tetrabenzoylethylene were isolated, and in the second case tribenzoylmethane, thus providing indirect confirmation of the proposed scheme, since the dibenzoylmethane and tribenzoylmethane must have been formed from the respective radicals of dibenzoylmethyl and tribenzoylmethyl.

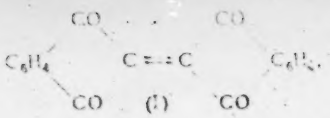
The results obtained prompted us to undertake the reaction of sodium diethyl phosphite and of triethyl phosphite with other halogenated derivatives containing two carbonyl groups in the α-position to the carbon linked with the halogen. We selected for this purpose bromoindandione and its derivatives. Bromoindandione reacts smoothly with triethyl phosphite and is reduced to indandione:



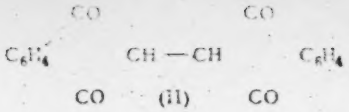
This reaction course is confirmed by the action of metallic sodium on bromoindandione in a toluene medium which leads to indandione:



The reaction between bromoindandione and sodium diethyl phosphite is more complicated. Diphthalylethene (I) and diphthalylethane (II) are evidently formed.

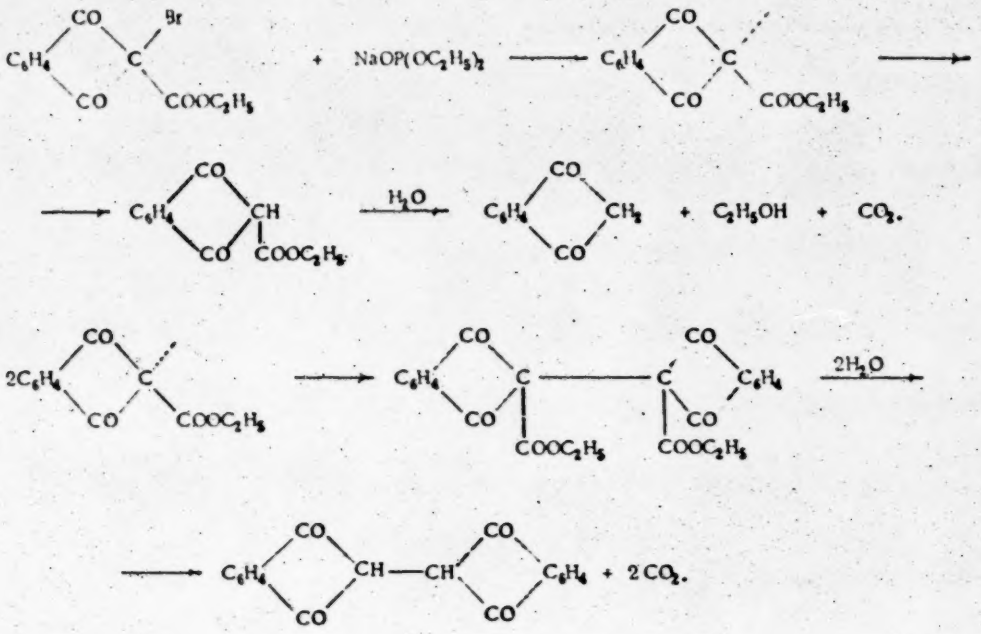


(I)

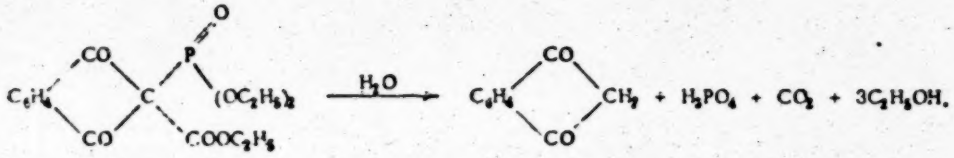


(II)

We have investigated the action of sodium diethyl phosphite and triethyl phosphite on ethyl bromoindandionecarboxylate. Indandione and diphthalylethane were isolated. In the present stage of the investigation the most probable explanation of this reaction course involves the formation of the free radical of the ester of indandionecarboxylic acid and the dimerization of the radical; alternatively reaction might take place with hydrogen donors (in this case the ester) followed by saponification of the ester and cleavage of carbon dioxide from the free acid:

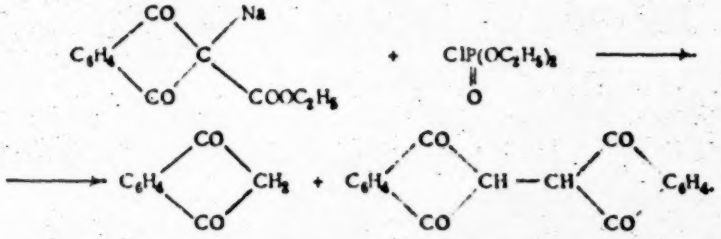


The possibility is not excluded, however, of formation of indandione as a result of saponification of the phosphoric ester since β-ketophosphonic acids are hydrolyzed with formation of a carbonyl compound and phosphoric acid [6]:



With triethyl phosphite, ethyl bromoindandionecarboxylate forms indandione.

It is interesting to note, as our experiments showed, that when the sodium salt of ethyl indandionecarboxylate reacts with diethylphosphorous acid chloroanhydride, indandione and diphthalylethane are formed:



Additional investigations are required for a conclusive explanation of the mechanism of the unusual reactions which we have described.

EXPERIMENTAL

Reaction of dinaphthylchlorobromomethanes and of 9-bromo- and 9-chlorofluorines with sodium diethyl phosphite and with triethyl phosphite

Attempts to effect the reactions between dinaphthylchloro- and bromomethanes and 9-chloro- and 9-bromofluorines and sodium diethyl phosphite in a medium of dry ether, benzene and dioxane, even in some cases in a sealed tube at a temperature of 130-140°, did not lead to any products whatsoever. The starting substances were recovered unchanged. The same must be said about the reactions of the above-mentioned compounds with triethyl phosphite. These reactions do not proceed either with or without solvents.

Reaction of sodium diethyl phosphite with 9,10-dibromophenanthrene

To a solution of sodium diethyl phosphite (2 moles) (100 ml absolute ether, 14 g diethyl phosphorous acid and 2.3 g metallic sodium) was added 15.7 g finely pulverized 9,10-dibromophenanthrene with m.p. 97-98°. Within a few minutes after the start of gradual addition of the latter; violent boiling occurred and did not cease until all had been added. Sodium bromide came down. The liquid portion was collected and the ether driven off to leave a crystalline precipitate with m.p. 92-93° (after recrystallization from absolute ethanol) in amount of 7.3 g (60% of the theoretical). This was identified as phenanthrene. A mixed test with phenanthrene did not give a melting point depression.

After removal of the phenanthrene, the liquid was vacuum distilled to give a product with b.p. 79-81° (12 mm) in a yield of 63.1%. This fraction had the constants d_{20}^{20} 1.0779; n_D^{20} 1.4095; readily reactive with metallic sodium. Its constants agreed best with those of diethyl phosphorous acid.

Reaction of 9,10-dibromophenanthrene with triethyl phosphite

To 19 g dry 9,10-dibromophenanthrene was added 18.6 g triethyl phosphite. No signs of reaction were observed at the ordinary temperature. Heating was carried out for 2 hours on a boiling water bath and the reaction mass acquired the color of bromine. After an hour's heating ethyl bromide began to come off at a temperature of 38-40°. The weight of the ethyl bromide was 4 g (66.6% of the theoretical). The color of the reaction mass became progressively lighter as the ethyl bromide was evolved.

Fractionation in vacuum yielded three fractions. The last fraction, which came over at 176° (5 mm), rapidly crystallized. The crystals had m.p. 97-98° and did not give a depression in admixture with phenanthrene. Yield 8.85 g (93.33% of the theoretical). The identity of the product was confirmed by formation of the picrate which melted at 145° in agreement with the literature.

The first two fractions were redistilled to give:

Fr. I., b.p. 46-63° (8 mm), 2.2 g; d_{20}^{20} 1.0400; n_D^{20} 1.4120
Fr. II., b.p. 63-65° (8 mm); 5.6 g (72% of the theoretical), d_{20}^{20} 1.0740; n_D^{20} 1.4107

The constants of Fraction II correspond to those of diethyl phosphorous acid.

Reaction of sodium diethyl phosphite with dibenzoylbromomethane

A solution of 9 g dibenzoylbromomethane [7] in 10 ml dry benzene was run into sodium diethyl phosphite (75 ml dry ether, 4.2 g diethyl phosphorous acid and 0.68 g metallic sodium). Slight heat was developed during the reaction, and the reaction mass was afterwards heated for 2 hours on a water bath. White crystals were isolated after filtering off the precipitated sodium bromide and driving off the ether.

After two recrystallizations from methanol the crystals melted at 77-78°. A mixed test with dibenzoylbromomethane shows a melting point depression, but the mixture with dibenzoylmethane does not show a melting point depression. Yield of dibenzoylmethane 69.1% of the theoretical. This reaction, when carried out in a medium of dry benzene, presented the same features except that the yield of dibenzoylmethane was lower (42.7%).

Reaction of dibenzoylbromomethane with triethyl phosphite

Dropwise addition of 4.76 g triethyl phosphite was made to 8 g dibenzoylbromomethane. The reaction was violent and the temperature inside the flask rose to 80°. The white crystalline precipitate was separated from the

liquid portion; it had m.p. 77-78° and did not give a depression in a mixed test with debenzoylmethane. Yield of dibenzoylmethane 3.65 g (80.8% of the theoretical).

Reaction of sodium diethyl phosphite with tribenzoylbromomethane

A solution of sodium diethyl phosphite, prepared from 4.3 g diethyl phosphorous acid, 0.72 g metallic sodium and 75 ml dry ether, was run into 11.8 g dry, pulverized tribenzoylbromomethane [8], m.p. 114-115°. On running in the solution of sodium diethyl phosphite, an intense yellow coloration was developed and the temperature of the reaction mass rose to an extent sufficient to boil the ether. After the audition was completed, the reaction mass was heated for 2 hours on a water bath. A voluminous white precipitate was formed which melted at 226-228° after recrystallization from ethanol and did not give a depression in a mixed melting test with tribenzoylmethane. Yield 7 g (58.3% of the theoretical).

From the liquid portion was isolated 1.8 g of a fraction with b.p. 90-91° (8 mm); d_{20}^{20} 1.0766; n_D^{20} 1.4101.

Found %: P 16.97; C 39.64; H 8.18
Calculated %: P 17.03; C 39.59; H 8.22 $C_6H_{15}O_3P$.

In its constants and analysis the fraction is identical with triethyl phosphite [9].

Reaction of tribenzoylbromomethane with triethyl phosphite

4 g triethyl phosphite was run into 8.8 g dry tribenzoylbromomethane. Each drop reacted violently with the tribenzoylbromomethane, and the temperature of the reaction mass rose to 70-80° during the addition. The reaction then stopped and again restarted on addition of 50 ml dry ether. This was marked by commencement of boiling of the ether and by rise in temperature of the reaction mass. The white precipitate formed by the reaction was filtered off and purified; it had m.p. 226-228°. A mixed test with dibenzoylmethane did not give a melting point depression. Yield 3.6 g (56.6% of the theoretical).

From the filtrate was isolated a fraction with b.p. 78-79° (3 mm) in the amount of 1.2 g; constants d_4^{20} 1.0741; n_D^{20} 1.4070.

Found %: P 16.51, 16.29
Calculated %: P 17.03 $C_6H_{15}O_3P$.

The constants of this fraction correspond to those of triethyl phosphate.

Reaction of dibenzoylbromomethane with metallic sodium

2.4 g (3 moles) metallic sodium was placed in 70 ml dry toluene, and by very vigorous shaking while the toluene was heated sufficiently to melt the sodium, the latter was converted into a powder. Into the flask was then run 10 g dry dibenzoylbromomethane. Bubbles at once came off fairly energetically. The mixture was heated for 6 hours on a boiling water bath. A white precipitate was formed, the solution darkened to a brown color. The precipitate was filtered off together with the unreacted sodium and washed with dry toluene. The toluene solution was left to evaporate spontaneously; after removal of the resinous portion of the residue on a porcelain plate, 0.5 g dibenzoylmethane with m.p. 76-77° was separated.

2.5 g of an inorganic solid was isolated from the precipitate from the toluene solution after decomposition of the excess sodium with ethanol. From the solution, strongly acidified with 0.1 N HCl, was obtained a yellow precipitate which after recrystallization from ethanol melted at 180-185°, in agreement with the melting point in the literature [10] for tetrabenzoylethylene. Yield 0.3 g.

Reaction of tribenzoylbromomethane with metallic sodium

0.4 g (2 moles) metallic sodium was placed in 25 ml dry toluene. The toluene was heated to the boil and the metallic sodium reduced to powder. To the still hot toluene was added 3.4 g tribenzoylbromomethane. The reaction proceeded as with dibenzoylbromomethane. 2.4 g tribenzoylbromomethane was recovered unchanged. Tribenzoylmethane was isolated in extremely small amount.

Reaction of ethyl bromoindandionecarboxylate with sodium diethyl phosphite

Into a solution of sodium diethyl phosphite (5 g diethyl phosphorous acid, 0.8 g metallic sodium and 50 ml dry ether) was run a solution of 10 g ethyl bromoindandionecarboxylate [11] in absolute ether. A flocculent precipitate came down. The color of the reaction mass changed from orange to yellow, at times becoming dark-green. Heat was liberated during the reaction and the ether boiled. After the reaction mass had been

heated on a water bath for an hour, the yellow precipitate was separated, washed with ether and recrystallized from water; it then melted at above 215° with decomposition. According to the literature [12] it is identical with diphthalylethane. Yield 0.8 g.

From the filtrate at 112-115° (9-10 mm) was distilled off a liquid which soon crystallized to white, well-formed crystals with m.p. 132-134°; weight 2 g. A mixed test of these crystals with indandione did not give a melting point depression. A second experiment gave exactly the same results.

Reaction of ethyl bromoindandionecarboxylate with triethyl phosphite

4 g triethyl phosphite was added dropwise to 6 g dry ethyl bromoindandione carboxylate. The reaction was very violent; the temperature inside the flask rose to 85° and a reddish-brown liquid was formed. The reaction was conducted without supplementary heating. On standing white, acicular crystals came down with m.p. 130-132°. The melting point of a mixed sample with the product from the preceding experiments was 130-131°. Yield 4.9 g.

Reaction of the sodium salt of ethyl indandione carboxylate with diethyl phosphorous acid chloroanhydride

8 g diethyl phosphorous acid chloroanhydride was added dropwise to 10 g sodium salt of ethyl indandione carboxylate. The reaction was conducted with heating to the boiling point of the ester. The reaction mass was diluted with 30 ml dry ether and left overnight. The yellow precipitate was separated by dilution of the reaction mass with ethanol and purified; it melted at 215° with decomposition. Diphthalylethane was isolated; yield 7.5 g. The ethanolic filtrate was worked up to give acicular crystals with m.p. 134°. A mixed test of these crystals with indandione did not give a melting point depression.

Reaction of bromoindandione with sodium diethyl phosphite

To an ethereal solution of sodium diethyl phosphite, prepared from 3.5 g diethylphosphorous acid, 0.53 g metallic sodium and 50 ml dry ether, was added 6 g bromoindandione [11]. The reaction was vigorous and caused the ether to boil. No heat was applied. A precipitate came down which was insoluble in ether but partly soluble in ethanol. The ether-insoluble portion was gray-green in color and weighed 1 g; m.p. 370°. On the basis of the literature data [12], it may be assumed to be the sodium salt of diphthalylethane.

Evaporation of the ethereal filtrate left a black resin which after drying on a porous plate separated 0.35 g of red solid with m.p. 320-322° (with decomp.). On the basis of the same literature data [12] it may be regarded as diphthalylethene.

Reaction of bromoindandione with triethyl phosphite

1.5 g triethyl phosphite without a solvent was run into 1 g bromoindandione. The reaction was performed with use of temperature to the boiling point of triethyl phosphite. The reaction mass changed into a dark-brown liquid which was heated for 2 hours on an oil bath. After 24 hours crystals had been deposited — small white needles with a yellowish tinge. After recrystallization from alcohol-ether mixture they melted at 130-132°. A mixed test with indandione did not give a depression of melting point. Yield 0.5 g (75.7% of the theoretical). The composition of the isolated compound was confirmed by analysis.

Found %: C 73.36; 73.42; H 4.35; 4.35
Calculated %: C 73.56; H 4.11 $C_9H_6O_2$.

Reaction of bromoindandione with metallic sodium

2.5 g sodium (3 moles) was put into 50 ml dry toluene. The sodium was converted to powder in the boiling toluene. To the mixture of hot toluene and sodium powder was added 6 g bromoindandione. After heating on a water bath, bubbles began to come off. After 1.5 hours' heating on an electric hot plate at the boiling point of toluene, sodium bromide started to come down. The toluene solution was separated from the precipitate and the unreacted sodium. The sodium was dissolved by ethanol. The total weight of sodium bromide and sodium ethoxide was 5.15 g.

From the toluene solution was separated 3.7 g (95% of the theoretical) yellowish powder; after washing with water and thorough drying, it melted at 129-130°. A mixed test with synthetic indandione did not give a depression.

SUMMARY

1. Dinaphthylchloromethane, dinaphthylbromomethane, 9-chlorofluorine and 9-bromofluorine did not

react in the experimental conditions.

2. Phenanthrene was formed by reaction of sodium diethyl phosphite and triethyl phosphite with 9,10-dibromophenanthrene.

3. Dibenzoylbromomethane and tribenzoylbromomethane react with sodium diethyl phosphite or with triethyl phosphite with formation of dibenzoylmethane and tribenzoylmethane.

4. Bromoindandione and the ethyl ester of bromoindandionecarboxylic acid react with sodium diethyl phosphite or with triethyl phosphite with formation of indandione or of products of dimerization of the free indandionyl radical.

5. The most probable reaction scheme, which explains the anomalous course of the bromo compounds with sodium diethyl phosphite or triethyl phosphate, is one involving the assumption of formation of free radicals as intermediate products.

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* T.p. = C.B. Translation pagination.

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THE RELATIVE REACTIVITY OF THE METHYL GROUPS OF BENZO DERIVATIVES OF 4-METHYLPYRIDINE

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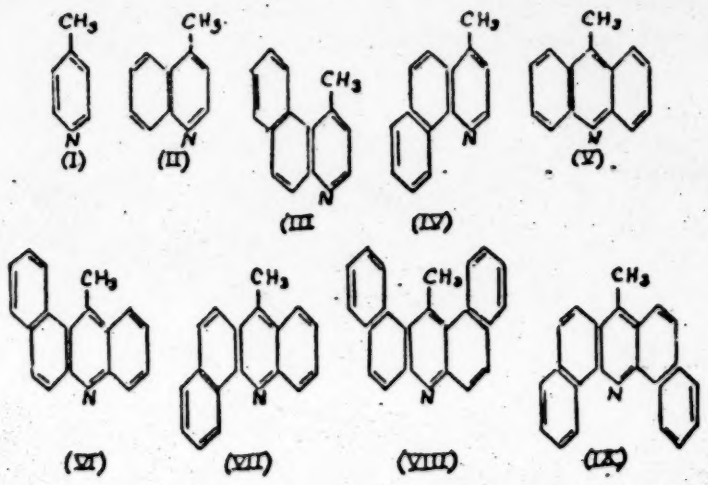
The methyl groups of nitrogen-containing heterocyclic compounds located in the α- or γ- position to the nitrogen possess, as we know, labile hydrogen atoms. This lability is manifested by the ability of such compounds to enter into reaction with aldehydes, ketones, aromatic nitroso compounds, diazo compounds, etc. The reactions with aldehydes proceed the most readily, while only few compounds are capable of coupling with diazo compounds.

Porai-Koshits and co-workers [1,2] showed that 9-methylacridine readily reacts with nitroso and diazo compounds, whereas α-and γ- picolines, quinaldine and lepidine [3] enter into these reactions only in the form of quaternary salts. Results of a study of the activity of methyl groups of benzo derivatives of 9-methylacridine, published previously by Porai-Koshits and one of us [4,5], show that the introduction of one, and in still greater measure, two angular condensed benzene rings into the molecule of 9-methylacridine lowers the reactivity of the methyl groups in reactions with aromatic aldehydes, nitrosodimethylaniline and diazo compounds.

In view of the high chemical activity of 9-methylacridine, it seemed of interest to throw more light on the influence of the number and position of the benzene rings upon the reactivity of methyl groups in six-membered nitrogen-containing heterocycles. Compounds of the quinoline series were included in the investigation. We studied the relative activity of the methyl groups of the following compounds: 4-methylpyridine (I), 4-methylquinoline (II), 4-methyl-5,6-benzoquinoline (III), 4-methyl-7,8-benzoquinoline (IV), 9-methylacridine (V), 9-methyl-1,2-benzacridine (VI), 9-methyl-3,4-benzacridine (VII), 9-methyl-1,2,7,8-dibenzacridine (VIII) and 9-methyl-3,4,5,6-dibenzacridine (IX). Their condensations with m-nitrobenzaldehyde were studied.



Condensation of the heterocyclic compounds with m-nitrobenzaldehyde was conducted with heating of equimolar amounts of the starting substances in presence of acetic anhydride in sealed tubes at 150-153° for 1.5 hours. The reactions resulted in formation of the corresponding styryl derivatives.

Due to the low mobility of the hydrogen atoms of the methyl groups of some of the investigated compounds, it was more convenient to evaluate the amount of reacted heterocycle not from the yield of styryl derivative but from the amount of unreacted m-nitrobenzaldehyde. The latter was separated from the heterocyclic compound by treatment of the reaction mass with hydrochloric acid followed by precipitation as the semicarbazone.

In addition the unreacted starting heterocyclic compound was extracted from the acidic solutions, and in some cases also the reaction product.

No great accuracy is claimed for our procedure for determination of the activity of the methyl groups of benzo derivatives of 4-methylpyridine; it only makes possible a relative evaluation of their reactivity. The results obtained are set forth in the table.

TABLE

Heterocyclic compound *	Amount of unreacted m-nitrobenzaldehyde, calculated as semicarbazone %	Observations
4-Methylpyridine	47.85	45% 4-(m-nitrostyryl)-pyridine isolated
4-Methylquinoline	79.8	14% 4-(m-nitrostyryl)-quinoline isolated
4-Methyl-5,6-benzoquinoline	94.0	
4-Methyl-7,8-benzoquinoline	92.11	
9-Methylacridine	43.74	Approximately 47% 9-(m-nitrostyryl)-acridine isolated
9-Methyl-1,2-benzacridine	80.39	
9-Methyl-3,4-benzacridine	76.10	
9-Methyl-1,2,7,8-dibenzacridine	88.82	
9-Methyl-3,4,5,6-dibenzacridine	94.10	Approximately 95% unreacted 9-methyl-3,4,5,6-dibenzacridine isolated

* The weight of sample of heterocyclic compound varied between 0.25 and 0.78 g; the weight of m-nitrobenzaldehyde in all cases was 0.4 g; the amount of acetic anhydride was 5 ml. The melting point of m-nitrobenzaldehyde semicarbazone was in the range of 226-231°.

The experimental data show that the most active of the compounds concerned in the reaction with m-nitrobenzaldehyde is 9-methylacridine; it is closely followed by γ-picoline. All the remaining compounds are considerably less reactive.

Special attention is merited by the reactivity of lepidine which, according to reports in the literature, should have occupied a position intermediate between γ-picoline and 9-methylacridine. Actually, however, in passing from one member to another in the series of benzologs of γ-picoline, no regular rise in reactivity is observed. The introduction of a benzene ring into the 2,3-position of γ-picoline causes a drop in the activity of the methyl groups of the heterocyclic compound. Increase of the complexity of the lepidine molecule by fusion with one benzene ring leads either to a rise of reactivity (as was the case with 9-methylacridine when a second benzene ring was fused to the heterocyclic nucleus) or to further depression of the reactivity (in the case of introduction of a benzene ring in the 5,6- or 7,8-position of lepidine).

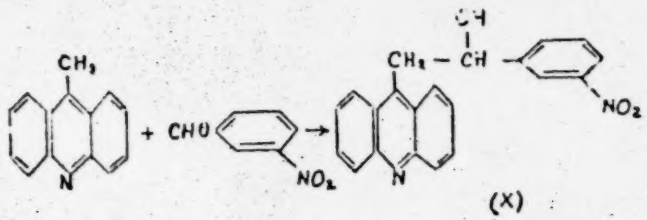
On passing from 9-methylacridine to its monobenzo derivative, a fresh fall in activity of the methyl group is observed, as exemplified by 9-methyl-1,2-benzacridine and 9-methyl-3,4-benzacridine. Still lower mobility is possessed by the hydrogen atoms of the methyl groups of the two isomers of 9-methyldibenzacridine which we investigated. 9-methyl-3,4,5,6-dibenzacridine is substantially lacking in reactivity with m-nitrobenzaldehyde in the specified conditions.

Comparison of the reactions of γ-picoline and lepidine with o-nitrobenzaldehyde again revealed the greater reactivity of the picoline.

At the same time we studied the photochemical reactions of benzo derivatives of lepidine and of 9-methylacridine with m-nitrobenzaldehyde. On carrying out the reactions of these compounds under the influence of ultraviolet rays, we expected the methylated heterocyclic compounds, due to their greater reactivity, to be more easily amenable to photochemical transformations than the corresponding aromatic hydrocarbons which are known to react with carbonyl compounds under the action of light. This process is usually accompanied by dehydrocondensation of the aromatic hydrocarbons or by a reaction of the type of the aldol condensation [6, 7].

We carried out the photochemical reactions by irradiating benzene solutions of equimolar amounts of m-nitrobenzaldehyde and 4-methylquinoline, 4-methyl-5,6-benzoquinoline, 9-methylacridine, and 9-methyl-1,2-

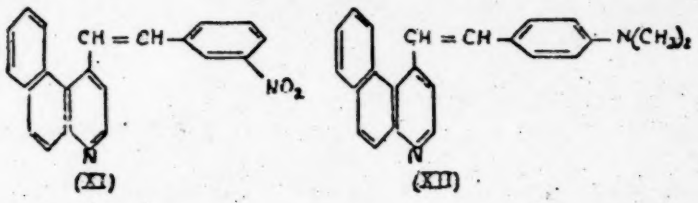
benzacridine with a PRK-2 lamp in a nitrogen atmosphere. The most active of the investigated compounds in photocondensations was again 9-methylacridine. The reaction between 9-methylacridine and m-nitrobenzaldehyde under the action of light is of the aldol condensation type with formation of α-(m-nitrophenyl)-β-(9-acridyl)-ethanol, the yield of which after 100 hours' irradiation was 54% of the theoretical.



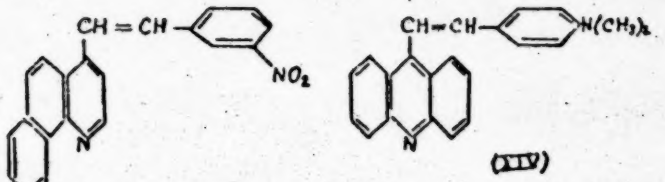
(X)

The remaining compounds do not react with m-nitrobenzaldehyde when irradiated with the mercury lamp for 100 hours. Nevertheless, in spite of the high reactivity of 9-methylacridine, we did not succeed in effecting its condensation with acetone, acetophenone, or benzophenone when exposed to the rays from the quartz mercury lamp. In these cases up to 90% of the original 9-methylacridine was recovered after irradiation of the mixture under ultraviolet rays for 150 - 180 hours.

In the quaternary salts of methylated heterocycles the methyl group is known to be considerably more active than in the free bases. Due to the low reactivity of the methyl groups of benzo derivatives of lepidine when used in the form of the free bases for the preparation of their styryl derivatives, we made use of the corresponding hydrochlorides. Thus, on heating 5,6-benzolepidine hydrochloride with m-nitrobenzaldehyde and p-dimethylaminobenzaldehyde in acetic anhydride, m-nitrobenzylidene-5,6-benzolepidine (XI) and p-dimethylaminobenzylidene-5,6-benzolepidine (XII) were obtained. Similarly we prepared m-nitrobenzylidene-7,8-benzolepidine (XIII):



(XI) (XII)



(XIII) (XIV)

In addition to these compounds we prepared 9-(p-dimethylaminostyryl)-2-methylacridine (XIV) by heating 2,9-dimethylacridine with p-dimethylaminobenzaldehyde in acetic anhydride.

EXPERIMENTAL

Starting Substances

Lepidine (II) was prepared by Mikhailov's method [8]. 9-Methylacridine (V) was prepared by the method of Porai-Koshits and Vernikovskaya [9]. After purification via the tartrate [10] it had m.p. 117.5°.

4-Methyl-5,6-benzoquinoline (III) was prepared by the method of Hamilton and Benson [11]; its hydrochloride was obtained by passing dry hydrogen chloride into a benzene solution of 4-methyl-5,6-benzoquinoline; it formed needles with m.p. 224-227°.

9-Methyl-1,2-benzacridine (VI), 9-methyl-3,4-benzacridine (VII) and 9-methyl-3,4,5,6-dibenzacridine (IX) were obtained by the previously described method [5, 6].

4-Methyl-7,8-benzoquinoline (IV) was previously obtained by Hamilton and Gobeil but we introduced some changes in the method. 2-Hydroxy-4-methyl-7,8-benzoquinoline was prepared by 15 minutes' heating of aceto-aceto-1-naphthylamide with concentrated sulfuric acid in a yield of 95.7%. Gibson [12] carried out this cyclization with the help of hydrochloric acid at room temperature. We failed to effect the transformation of 2-hydroxy-4-methyl-7,8-benzoquinoline into 2-chloro-4-methyl-7,8-benzoquinoline by the method of Hamilton and Gobeil [13]. In the conditions recommended by the authors we obtained a small amount of a substance with a wide melting range (130-200°), the main bulk was unchanged starting material. On increasing the amount of chlorinating agents 2.5 times and the duration of heating to 20 hours, 2-chloro-7,8-benzolepidine was obtained in a yield of 64.6% of the theoretical (the m.p. of 134° agrees with that of the authors cited). In the reduction of 2-chloro-4-methyl-7,8-benzoquinoline to 4-methyl-7,8-benzoquinoline it was again found necessary to use more tin and hydrochloric acid than was recommended by the previous authors [13] and to double the duration of heating of the mixture.

9-Methyl-1,2,7,8-dibenzacridine was prepared from 8,8-dinaphthylamine which was obtained by Cook's method [14], by heating 2-naphthol with 2-naphthylamine in presence of naphthalene-2-sulfonic acid, in a yield of 80%; m.p. 173-174°. 50 g (0.19 mole) 8,8-dinaphthylamine, 20 g (0.19 mole) acetic anhydride and 26 g anhydrous zinc chloride were heated for 5 hours at 185-199° (thermometer in the mixture). The reflux condenser was then put in the sloping position and the temperature raised to 250° to distil off the acetic acid. The mass was then heated for 30 minutes at 250-260°. The resultant dark, viscous resin was repeatedly treated with 10% sulfuric acid.

Neutralization of the acidic solution with 25% ammonia gave 25.5 g dark-yellow substance with m.p. 155-165°. Yield of crude product 46.8% of the theoretical. The precipitate was twice crystallized from benzene, then from ethyl acetate and then twice from ethanol. In this way yellow needles were obtained with m.p. 180-183°.

Found %: C 89.88; H 5.40; N 4.96
$C_{22}N_{15}N$. Calculated %: C 90.07; H 5.11; N 4.79

Chromatographic treatment of the precipitate with m.p. 155-165° on alumina gave, apart from the yellow substance with m.p. 180-183°, a small quantity of long, white silky needles with m.p. 215-216° with the following elementary composition:

Found %: C 90.02, H 5.40; N 4.81
$C_{22}H_{15}N$. Calculated %: C 90.07; H 5.11; N 4.79

Previously 9-methyl-1,2,7,8-dibenzacridine was obtained by the method of Bernthsen, and the author [15] points out that he obtained only one substance with m.p. 184-185°.

For study of the relative reactivity we selected the substance with m.p. 180-183°.

Investigation of Relative Reactivity of the Methyl Groups of Benzo Derivatives of 4-methylacridine

0.2471 g (0.0027 mole) γ-picoline and 0.4000 g (0.0027 mole) m-nitrobenzaldehyde were dissolved in 5 ml acetic anhydride and the mixture was heated in a sealed tube on an oil bath at 150-153° for 1.5 hours. After the reaction mass had cooled, the tube was opened, the solution was run into 15 ml benzene and transferred to a separating funnel, the tube was rinsed out with 5 ml benzene. To the benzene solution was added 30 ml of 6 N hydrochloric acid and the mixture vigorously shaken. The benzene layer was separated from the acid layer and the latter was again treated with 15 ml benzene.

The benzene extracts were combined, washed with water and dried over calcium chloride. The benzene was driven off in vacuum. The residual m-nitrobenzaldehyde in the flask was dried in a vacuum desiccator to constant weight. Yield 0.2188 g or 54.7% of unreacted m-nitrobenzaldehyde. The precipitate of aldehyde was dissolved in the same flask with 2 ml ethanol and to the ethanol solution was added a solution of 0.3 g semicarbazide hydrochloride in 1 ml water. The precipitate of m-nitrobenzaldehyde semicarbazone was filtered off, washed with a few drops of dilute ethanol and dried to constant weight at 100°. Yield 0.2625 g m-nitrobenzaldehyde semicarbazone with m.p. 225-230°, equivalent to 0.1906 g, or 47.85%, of unreacted aldehyde.

Excess of 25% ammonia was added to the acid layer. The resultant voluminous amorphous precipitate was drained, washed with water, and dried at 100° to constant weight. Yield 0.3 g substance (48.2% of the theoretical) with m.p. 139-142°. According to the literature 4-(m-nitrostyryl)-pyridine melts at 144° [16].

In the case of lepidine and acridine derivatives, shaking of a benzene solution with acid brought down a salt. The acidic solution and the precipitate were separated from the benzene solution and again shaken with 15 ml benzene; the precipitate was then filtered through a glass filter. The benzene and aqueous solutions in the filtrate were separated and further working-up was on the same lines as in the case of γ-picoline.

On condensation of γ-picoline with o-nitrobenzaldehyde the reaction mass was worked up in the same conditions as in the preceding experiment. From the benzene solution was obtained 0.1900 g unreacted o-nitrobenzaldehyde. 0.1742 g, or 43.7% of unreacted aldehyde was recovered in the form of its semicarbazone. Neutralization of the acidic layer with ammonia gave 0.29 g of substance (47% of the theoretical) with m.p. 95-101°. According to the literature 4-(o-nitrostyryl)-pyridine melts at 105° [16].

In the case of condensation of lepidine with o-nitrobenzaldehyde, operation in the same conditions led to separation from the benzene solution of 0.3657 g unreacted aldehyde; 0.3500 g, or 57.5% of unreacted o-nitrobenzaldehyde was obtained in the form of the semicarbazone. On neutralization of the acidic solution with excess of 25% ammonia, 0.455 g, or 6.2%, o-nitrobenzylidenelepidine was obtained with m.p. 161-165°. According to the literature the m.p. is 172-173° [17].

Condensation of 9-Methylacridine with m-Nitrobenzaldehyde under the Action of Ultraviolet Rays

1.34 g (0.007 mole) 9-methylacridine and 1.05 g (0.007 mole) m-nitrobenzaldehyde were dissolved in 14 ml benzene (thiophene-free) in a molybdenum glass flask. The air above the liquid was displaced by nitrogen. The solution was irradiated with a PRK-2 lamp for 100 hours. At the conclusion of this period 1.3 g reaction product with m.p. 130-134° was filtered off from the solution. After two crystallizations from benzene and then from dioxane, the substance was obtained in the form of fine, yellow needles with m.p. 146.5-147.5°.

Found %: N 8.10

$C_{21}H_{16}O_3N$. Calculated %: N 8.14

This compound was previously prepared by Sharp and co-workers [19] by heating 9-methylacridine with m-nitrobenzaldehyde at 100° in the absence of condensing agents. The authors reported m.p. 145° [19].

m-Nitrobenzylidene-5,6-benzolepidine (XI)

0.5 g (0.0022 mole) 5,6-benzolepidine hydrochloride and 0.33 g (0.0022 mole) m-nitrobenzaldehyde were dissolved in 1.5 ml acetic anhydride and heated at the boil for 3 hours. At the end of the heating the color of the solution had changed from yellow to reddish-yellow. Water (10 ml) and 25% ammonia were added to the cooled reaction mass until the reaction was alkaline to litmus; a white, oily precipitate came down. This was twice washed with ethanol (3 ml each time). Yield 0.21 g m-nitrobenzylidene-5,6-benzolepidine in the form of yellowish needles with m.p. 144-149°. Yield 30% of the theoretical. After crystallization from ethanol the m-nitrobenzylidene-5,6-benzolepidine formed white, silky needles with m.p. 168-169°. The product is soluble in the common organic solvents.

Found %: C 77.20; H 4.57

$C_{21}H_{14}O_2N_2$. Calculated %: C 77.29; H 4.32

m-Nitrobenzylidene-7,8-benzolepidine (XIII)

1 g (0.0044 mole) 7,8-benzolepidine hydrochloride and 0.65 g (0.0044 mole) m-nitrobenzaldehyde were dissolved in 5 ml acetic anhydride and the mixture boiled for 3 hours. After cooling, the solution was run into 5 ml water; a yellow oil formed and crystallized after a short time. The precipitate was washed 3 times with a small amount of methanol at room temperature (0.31 g, yield 21.8% of the theoretical). After three recrystallizations from methanol and then from ethanol, m-nitrobenzylidene-7,8-benzolepidine formed fine, white needles with m.p. 155-157°. The compound is readily soluble in the common organic solvents.

Found %: N 9.06

$C_{21}H_{14}O_2N_2$. Calculated %: N 8.68

p-Dimethylaminobenzylidene-5,6-benzolepidine (II)

1 g (0.0044 mole) 5,6-benzolepidine hydrochloride and 0.65 g (0.0044 mole) p-dimethylaminobenzaldehyde were dissolved in 3 ml acetic anhydride and the mixture boiled for 2 hours. At the end of the heating the color of the solution had become cherry-red. After addition of 10 ml water and 5 ml 25% ammonia to the reaction mass,

a red amorphous precipitate came down. This was filtered off, washed with water and dissolved wet in 5 ml ethanol. The product was reprecipitated from the ethanol solution by addition of 8 ml 20% sodium hydroxide. The orange precipitate was recrystallized from 20 ml ethanol to give 0.38 g (26.9% of the theoretical) of yellow needles. After two crystallizations from ethanol, p-dimethylaminobenzylidene-5,6-benzolepidine formed lemon-yellow needles with m.p. 170.5-171.5°.

Found %: N 9.06

$C_{21}H_{14}ON_2$. Calculated %: N 8.68

9-(p-Dimethylaminostyryl)-2-methylacridine (XIV)

2,9-Dimethylacridine was prepared by the method of Bonna [18]. 0.32 g (0.0015 mole) 2,9-dimethylacridine and 0.23 g (0.0015 mole) p-dimethylaminobenzaldehyde were dissolved in 2 ml acetic anhydride and heated for an hour at the boil. At the end of the heating the color of the solution had become dark-brown. After cooling, 0.18 g orange precipitate with m.p. 210-217° was filtered off from the solution. From the mother liquor after neutralization with ammonia was separated a further 0.3 g substance with m.p. approximately 204°. Yield of unpurified product 94% of the theoretical. After crystallization from methanol and then from a mixture of benzene and ligroine, 9-(p-dimethylaminostyryl)-2-methylacridine formed elongated orange rhombs with m.p. 225-226°. The compound dissolves readily in alcohols and benzene.

Found %: N 8.41

$C_{24}H_{22}N_2$. Calculated %: N 8.28

SUMMARY

1. An investigation was made of the lability of the hydrogen atoms of the methyl groups of 4-methylpyridine (I), 4-methylquinoline (II), 4-methyl-5,6-benzoquinoline (III), 4-methyl-7,8-benzoquinoline (IV), 9-methylacridine (V), 9-methyl-1,2-benzacridine (VI), 9-methyl-3,4-benzacridine (VII), 9-methyl-1,2,7,8-dibenzacridine (VIII) and 9-methyl-3,4,5,6-dibenzacridine(IX) in condensation reactions with m-nitrobenzaldehyde. A study was made of the photochemical reactions of the above compounds with carbonyl compounds.

2. It was found that in the condensations of the above compounds with m-nitrobenzaldehyde the activity of the methyl groups falls off on the one hand in the order: (I), >(II), >(III), ≥(IV), and on the other hand in the order: (V), > (VII), ≥ (VI), > (VIII), > (IX).

3. It was shown that, contrary to previously recorded views, the introduction of a benzene ring into the 4-methylpyridine molecule leads to a decline in the reactivity of the methyl group in condensation with o- and m-nitrobenzlaldehydes.

4. It was established that the most active of the investigated compounds toward m-nitrobenzaldehyde is 9-methylacridine. Passage from 9-methylacridine to its angular monobenzo derivatives (9-methyl-1,2- and 9-methyl-3,4-benzacridine) is accompanied by a fall in the reactivity of the methyl group. The activity of the methyl group is depressed to a still greater extent in the reaction of m-nitrobenzaldehyde with the angular dibenzo derivatives of 9-methylacridine.

5. It was established that the activity of the methyl group of benzo derivatives of 4-methylpyridine depends not only on the number of benzene rings but also on their position relative to the heterocyclic nucleus. This is particularly marked in the increased reactivity of 9-methylacridine and the low reactivity of the 5,6- and 7,8-benzo derivatives of 4-methylquinoline.

6. The great reactivity of 9-methylacridine in comparison with 5,6- and 7,8-benzo derivatives of lepidine is confirmed by the results of photocondensations of these compounds with m-nitrobenzaldehyde.

7. Several new styryl derivatives of the quinoline series were synthesized.

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COMMUNICATION 2. SPECTRAL INVESTIGATIONS OF ALCOHOLIC SOLUTIONS OF CHLORO DERIVATIVES OF ANILINE

A. A. Kharkharov

In spite of the great industrial importance of halogenated aniline derivatives, their ultraviolet spectra have been relatively little studied. It is known that the introduction of a chlorine atom into aniline in the ortho-position to the amino group has little influence upon the field of absorption. The maxima of the main bands of p-chloroaniline and of 2,4-dichloroaniline [1] are appreciably shifted in the direction of long waves in comparison with the maxima of o-chloroaniline and aniline [2 - 10]. We decided to make a systematic study of the spectra of alcoholic solutions of mono-, di-, tri- and tetrachloro derivatives of aniline with the aim of establishing a possible influence of the accumulation of substituents upon the form of the spectral curve and the position of the maxima.

Our investigations have shown that the spectra of all the chloro derivatives of aniline in the wave-length region of 210 to 800 mμ consist of two principal adjacent absorption bands. The intensity of the short-wave band is greater than that of the long-wave band. Due to the short-wave bands being relatively little altered both by accumulation of substituents and by change in the position of substituents, we limited ourselves to a comparison of the maxima of the long-wave bands.

For monochloro derivatives of aniline (Fig. 1, Table 1) the long-wave maxima are distributed in the sequence:

para > ortho > meta

This proves that the cause of the bathochromic displacements must be sought not only in the inductive influence of the halogen but also mainly in the possibility of development of fields of conjugation. Since the halogen in the para- position to the amino group is separated from the amino group by the longest conjugated chain of carbon atoms, its bathochromic action is the most intense. The halogen in the ortho- position has a considerably weaker effect. In view of the fact that the substitutents in the meta- position are not conjugated with one another, the repulsion of electrons of the amino group by the chlorophenyl residue will be least in this case.

EXPERIMENTAL

The spectral investigations were carried out with the SF-1 photoelectric spectrophotometer in the range of 210 to 700 mμ. The solvent was 96% ethanol. A solvent effect was excluded. All the substances were thoroughly purified (recrystallization from various solvents to constant melting point or distillation in vacuum). Identical concentrations of substances were used throughout.

On passing from monohalogenated to dihalogenated derivatives of aniline, further shifts of the absorption bands are observed in the long-wave direction (Figs. 1,2,3 and Table 1). Of the three dichloro derivatives of aniline that we investigated (1,2,5-; 1,3,4-; 1,2,4-) the greatest bathochromic displacement of the main absorption band occurs with the 1,2,4-isomer (Fig. 2, Table 1). The two other isomers have the same absorption maximum (Table 1, Figs. 2 and 3).

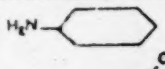
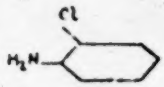
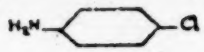
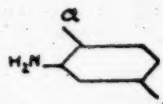
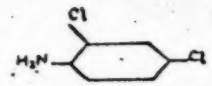
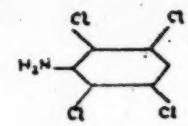
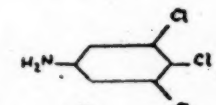
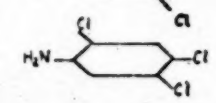
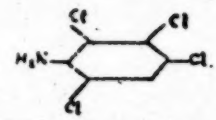
A further bathochromic displacement of the maximum of the main absorption band occurs on introduction into the aniline molecule of three and four atoms of chlorine (Figs. 4 and 5, Table 1), but their absorption likewise does not extend outside the ultraviolet region. 2,4,5-Trichloroaniline (λ_{max} 313 mμ) has a maximum at a longer wave length than 3,4,5-trichloroaniline (λ_{max} 310 mμ). Of the two tetrachloro derivatives that we investigated, 2,3,-4,6-tetrachloroaniline has a higher value of absorption maximum than 2,3,5,6-tetrachloroaniline (Fig. 6, Table 1).

In the order of increase of magnitude of the absorption maxima, the chlorinated anilines follow a definite sequence (see formulas on page 740).

A study of the additivity of the effect of substituents seemed to us of considerable theoretical interest. With this objective we compared the observed results for shifting of the main absorption band of di- and higher-substituted anilines with the results calculated by addition of the respective displacements of monohalosubstutited anilines (Table 1, Figs. 3 to 7). It was found that there is relatively slight deviation from additivity in the case of halogenated derivatives of aniline. The biggest deviation from additivity (−5 mμ) characterizes 2,4-dichloroaniline (Table 1)

TABLE 1

Main Absorption Maxima of Alcoholic Solutions of Chloro Derivatives of Aniline

No.	Amine	Formula of amine	Main absorption band in mμ	Shift of maximum, in mμ		Deviation in mμ
				Found	Calculated	
1	Aniline		285	–	–	–
2	m-Chloroaniline		288	3	–	–
3	o-Chloroaniline		293	8	–	–
4	p-Chloroaniline		300	15	–	–
5	2,5-Dichloroaniline		300	15	11	4
6	3,4-Dichloroaniline		300	15	18	–3
7	2,4-Dichloroaniline		303	18	23	–5
8	2,3,5,6-Tetrachloroaniline		308	23	22	1
9	3,4,5-Trichloroaniline		310	25	21	4
10	2,4,5-Trichloroaniline		313	28	26	2
11	2,3,4,6-Tetrachloroaniline		317	32	34	–2

Deviations of a similar order of magnitude are found for 3,4- and 2,5-dichloroanilines (–3 and 4 mμ), also for 2,3,4,6- and 2,3,5,6-tetrachloroanilines (–2 and 1 mμ), but the deviations are respectively of opposite sign). In the case of the trichloroderivatives the greatest observed deviation of the main absorption maximum from the calculated value occurs with the 3,4,5-isomer (Table 1, Figs. 1 to 7).

SUMMARY

1. Absorption spectra of alcoholic solutions of mono-, di-, tri- and tetrachloroanilines were investigated.

2. It was shown that there is a regular shift of the maximum of the main absorption band in the direction of longer wave lengths with increasing number of substituents.

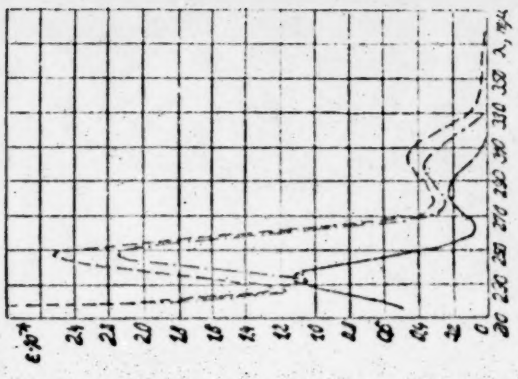


Fig. 3. Absorption spectra of alcoholic solutions of: – aniline; – – 2,4-dichloroaniline; –·– 3,4-dichloroaniline

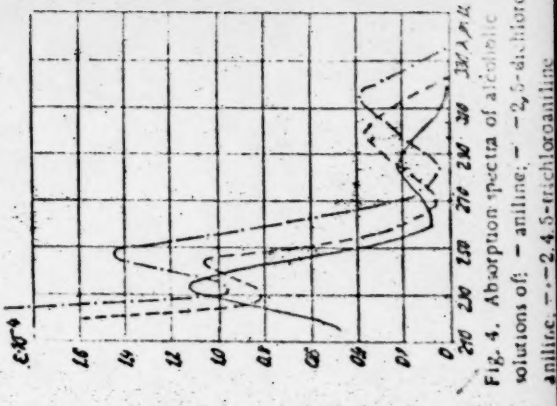


Fig. 4. Absorption spectra of alcoholic solutions of: – aniline; – – 2,5-dichloroaniline, –·–·– 2,4,5-trichloroaniline

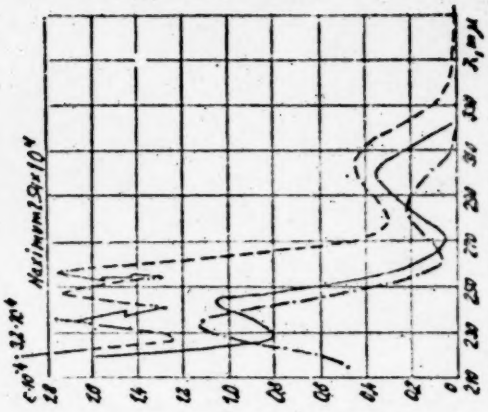


Fig. 2. Absorption spectra of alcoholic solutions of: – – 2,5-dichloroaniline; –·– 2,4-dichloroaniline; –··– aniline

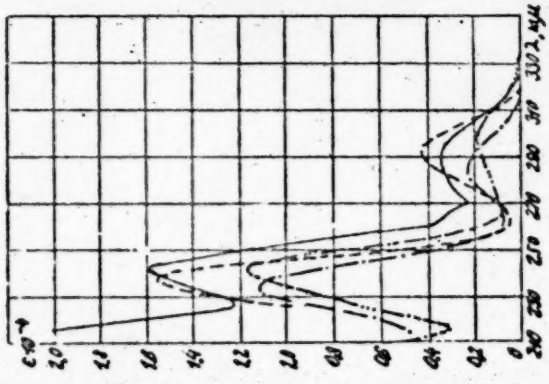


Fig. 1. Absorption spectra of alcoholic solutions of: – – ortho-chloroaniline; – meta-chloroaniline; –·– aniline; –··– para-chloroaniline

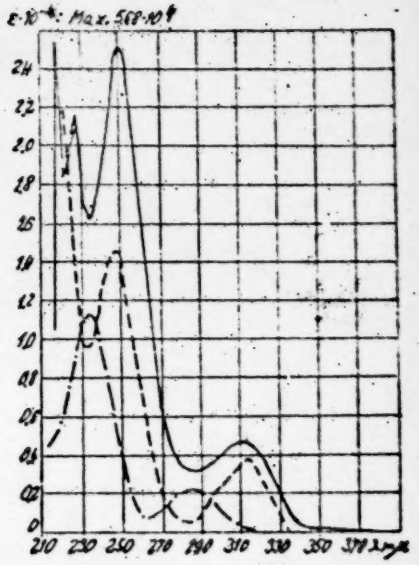


Fig. 5. Absorption spectra of alcoholic solutions of: – – 2,4,5-trichloroaniline, – 3,4,5-trichloroaniline, –·– aniline

3. It was established that chlorine atoms bring about a relativeiy small deviation from the addivity of the effect of the substituent. The magnitude of this deviation depends upon the number and position of the substituents.

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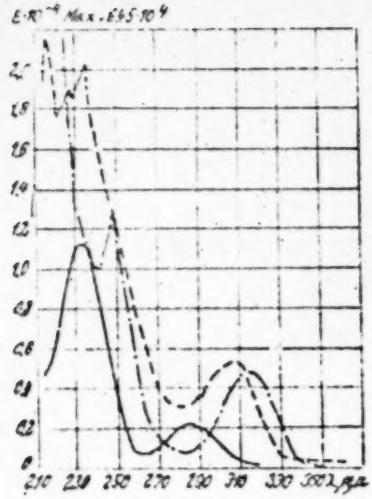


Fig. 6. Absorption spectra of alcoholic solutions of: —aniline, – – –2,3,5,6-tetrachloroaniline; –·–2,3,4,6-tetrachloroaniline.

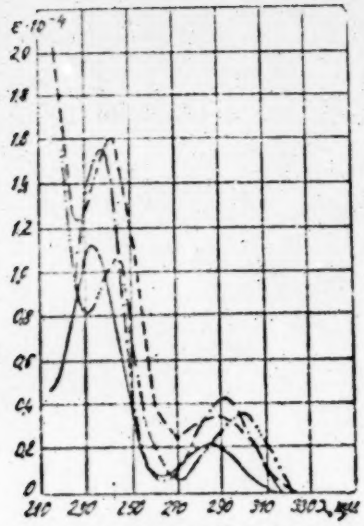
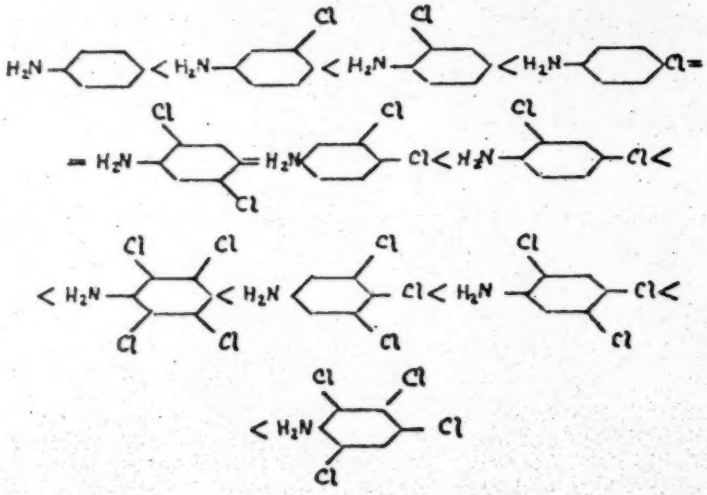


Fig. 7. Absorption spectra of alcoholic solutions of: —aniline; – – –meta-chloraniline; –·–ortho-chloroaniline; –··–2,5-dichloroaniline.



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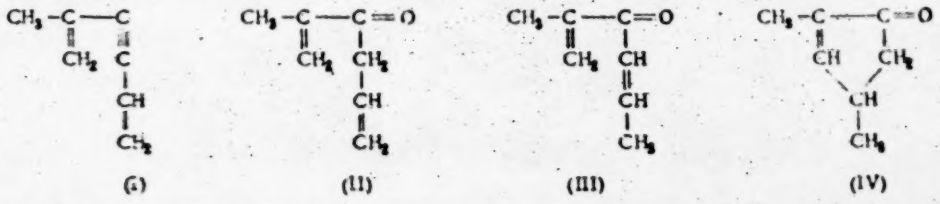
INVESTIGATION OF THE MECHANISM OF THE CYCLIZATION REACTION WITH THE HELP OF DEUTERIUM

COMMUNICATION 3

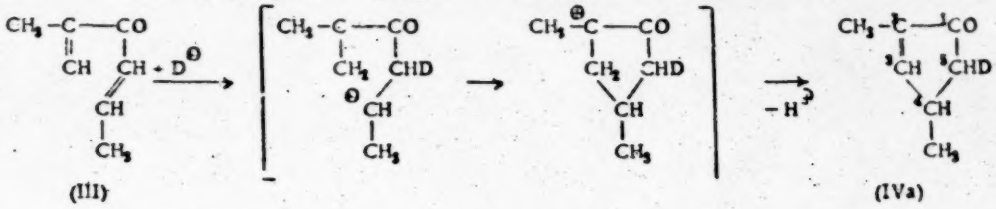
D. N. Kursanov, Z. N. Parnes, I. I. Zaretskaya and I. N. Nazarov

In the preceding communications [1, 2, 3] it was shown that the dienone formed by hydration of vinylisopropenylacetylene (I) cyclizes under the influence of acids to dimethylcyclopentenone (IV) by the ionic intermolecular mechanism proposed by Nazarov [4]. In this connection it was established that not only allylisopropenyl ketone (II) but also the isomeric propenylisopropenyl ketone (III) undergoes cyclization [3].



(I) (II) (III) (IV)

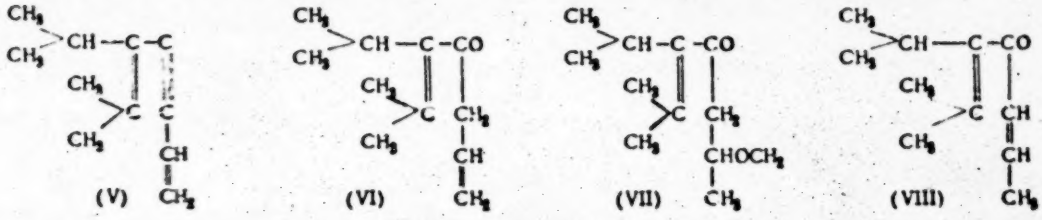
The ionic mechanism of cyclization of the dienone (III) into the cyclopentenone (IV) was verified by the method of labeled atoms with the help of deuterium [3]. Cyclization was effected with deuterophosphoric acid, and this gave monodeutero-dimethylcyclopentenone (IVa) which contains all the deuterium at the fifth carbon atom:



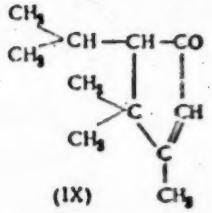
(III) (IVa)

As was shown by Nazarov and co-workers [5], also dienones of the type of (III) are easily amenable to cyclization. These compounds do not contain hydrogen atoms in the vinyl group at the end of the chain. In this case the resultant cyclopentenones contain a double bond at the 4,5-position.

We selected the dienone (VIII) for a study of the mechanism of cyclization of this type with the help of deuterium. This dienone is formed by hydration of the dienyne (V) under the influence of mercuric sulfate in aqueous methanol followed by cleavage of methanol from the methoxy ketone (VII) with the help of p-toluenesulfonic acid.



(V) (VI) (VII) (VIII)



(IX)

Cyclization of ketone (VIII), as shown by Nazarov and Pinkina [6], leads to trimethylisopropylcyclopentenone (IX).

The object of our investigation was to establish, when using deuterophosphoric acid for the cyclization of the initial dienone, whether the reaction proceeds by an intramolecular or by an ionic intermolecular mechanism. In the latter event, it was also desired to determine the point of introduction of deuterium into the molecule

of the resultant cyclic ketone (IX). The ionic intermolecular mechanism of cyclization of the initial dienone to the cyclopentenone (IX) could be rigorously demonstrated with the help of deuterium since monodeutero-cyclopentenone is formed on cyclization with deuterophosphoric acid.

That deuterium is actually introduced into the molecule of the cyclopentenone (IX) in the process of cyclization of the initial dienone (VIII) and not by way of deuterium exchange of these compounds was proved by special experiments. In the conditions of cyclization the cyclopentenone (IX) enters into exchange reaction with the deuterium-containing phosphoric acid only to a very slight extent, as can be seen from Table 1.

TABLE 1

Calculated for exchange of 1 H, in γ	Deuterium found, in γ	Exchange, in %
1060	110	10
1030	70	7

Consequently, the cyclopentanone (IX) enters into exchange reaction in the conditions of cyclization to the extent of not more than 7-10% of that calculated for exchange of one hydrogen atom.

The exchange capacity of the initial dienone (VIII) proved to be still smaller, as was established by special experiments on incomplete cyclization of this dienone with deuterium-containing phosphoric acid. In these experiments the unreacted dienone (VIII) and cyclopentenone (IX) were fractionated in a column of 25 theoretical plates and then analyzed for their deuterium content. The results are given in Table 2.

TABLE 2

Exp't. No.	Deuterium found, in γ: dienone (VIII)	cyclic ketone (IX)	Calc'd for exchange of 1 H, in γ
1	40	240	920
2	35	245	1050

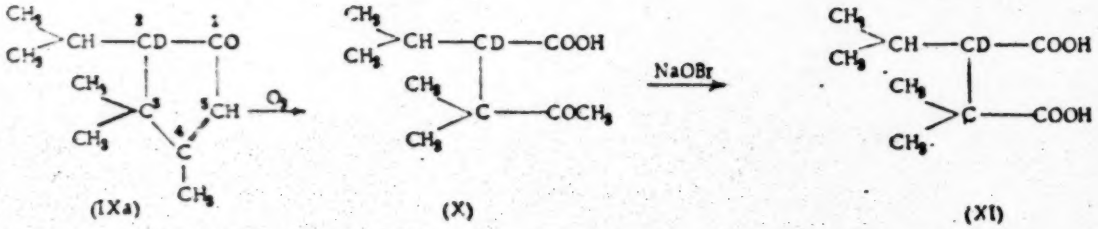
As we see from Table 2, the initial dienone (VIII) recovered after partial cyclization experiments contained a negligible amount of deuterium, whereas the cyclic ketone (IX) was considerably enriched in deuterium which was introduced during the cyclization process from the deuterium-enriched phosphoric acid.

The position of the deuterium in the cyclopentenone (IXa) was established by its ozonization to the ketoacid (X) which was then oxidized with bromide lye to dimethylisopropylsuccinic acid (XI). It was found that nearly the whole of the deuterium present in the cyclopentenone was retained in the dimethylisopropylsuccinic acid.

The deuterium content of the initial cyclopentenone (IXa) and of the acid (XI) obtained by ozonization and oxidation can be seen from the following data:

	Found deuterium in γ
Cyclic ketone (IXa)	70 100
Acid (XI)	62 100

It follows from these data that the deuterium introduced during the process of cyclization is present in the cyclic ketone (IXa) substantially entirely at C_2.



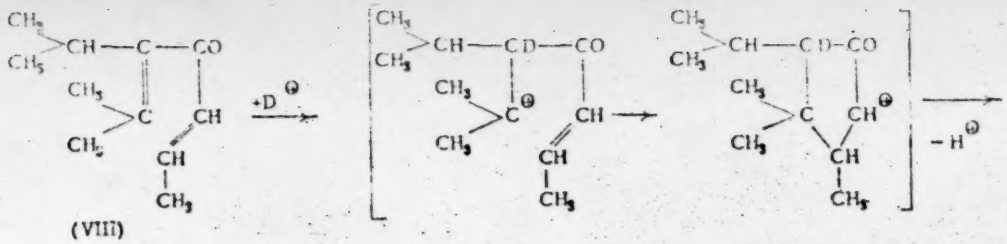
(IXa) (X) (XI)

The results obtained show that the dienone undergoing cyclization has the divinyl structure (VIII) and not the vinylallyl structure (VI), corresponding to the normal course of hydration of the initial dienyne (V). These experimental data lead to the following scheme for the mechanism of the cyclization reaction: (see following page)

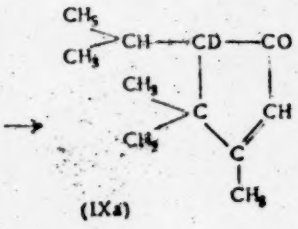
EXPERIMENTAL

Analyses for deuterium content were performed by the previously described method [7].

Preparation of dienone (VIII). The dienyne (V) was hydrated in aqueous methanol and methanol was split off from the 2-methoxy-5-isopropyl-6-methyl-5-hepten-4-one (VII) by heating with p-toluenesulfonic acid [6].



(VIII)



(IXa)

Distillation from a Favorsky flask gave a substance with b.p. 94-98° (12 mm); n_D^{20} 1.4715. The substance was then fractionated in a column packed with single glass helices with an efficiency of 25 theoretical plates. In this way from 44 g crude product was obtained 31 g pure dienone with b.p. 93-93.5° (12 mm), n_D^{20} 1.4735, d_4^{20} 0.8799, found MR 52.9; calculated MR 52.0. This dienone was used by us in the cyclization experiments.

Cyclic ketone (IX). The cyclic ketone (IX) was prepared by cyclization of dienone (VIII) with phosphoric acid (sp. gr. 1.76) as previously described [6]. The substance obtained had b.p. 98-100° (10 mm), n_D^{19} 1.4760. 40 g of this product was fractionated in the above-mentioned column to give 33 g pure cyclic ketone (IX) with b.p. 112-112.5° (17 mm); n_D^{20} 1.4779; d_4^{20} 0.9245. This ketone was used in experiments on the investigation of deuterium exchange.

Investigation of exchange ability of the cyclic ketone (IX). To 5.1 g cyclic ketone (IX) was added (from a dropping funnel) 5.55 g deuterium-enriched phosphoric acid (98%) with an excess density of 22,200 γ. After 2 hours' contact the mixture was gradually run into a solution of sodium bicarbonate and the cyclic ketone was extracted with ether. After drying the ethereal solution, driving off the ether and distilling the product in vacuum, 4.5 g cyclic ketone (IX) was obtained with b.p. 93° (8 mm). The water of combustion of this ketone had an excess density of 710 γ instead of the 1080 γ calculated for exchange of one atom of hydrogen.

Partial cyclization of ketone (VIII). To 23.0 g dienone (VIII) was gradually added, with cooling and stirring, 21.25 g deuterium-enriched phosphoric acid (98%) with an excess density of 22,200 γ. After 2 hours' contact the product was treated with bicarbonate solution and the ethereal solution was dried. After driving off the ether, the mixture was fractionated in a column to give the following fractions:

Fraction I, b.p. 89.1-89.4° (12 mm); n_D^{20} 1.4729; 4.5 g
Fraction II, b.p. 91.0-91.4° (12 mm); n_D^{20} 1.4732, 2.0 g
Fraction III, b.p. 91.4-101.2° (12 mm); n_D^{20} 1.4750; 1.5 g
Fraction IV, b.p. 101.2-102.8° (12 mm); n_D^{20} 1.4777; 6.5 g

Fraction IV is the cyclic ketone (IX). The water of combustion of this ketone had an excess density of 240 γ. Fraction I is the original dienone (VIII). Its water of combustion had an excess density of 26 γ. The excess density of the water of combustion of Fraction III was 50 γ. Calculated for exchange of one atom of hydrogen 1050 γ. Similar results were obtained on repeating this experiment – the excess density of the water of combustion of the cyclic ketone (IX) was 240 γ, that of dienone (VIII) was 40 γ, calculated for exchange of one atom of hydrogen 920 γ.

Monodeutero-cyclopentenone (IXa). Components for the cyclization were 14.4 g dienone (VIII) and phosphoric acid prepared from 9.6 g phosphorus pentoxide and 4.4 g deuterium oxide. Cyclization was carried out, as usual, at 20-21° for 8 hours. After working up in the usual way, the mixture was distilled from a Favorsky flask to give 12 g cyclic ketone (IXa) with b.p. 113-114° (18 mm); n_D^{20} 1.4776. A sample of this ketone was examined for its deuterium content. The excess density of the water of combustion was equal to 3895 γ. Since the water of combustion was diluted 18 times with the hydrogen-atoms present in the molecule, the excess density of one introduced hydrogen was equal to 3895 · 18 = 70,100 γ.

Ozonization of monodeutero-cyclopentenone (IXa). Ozonized oxygen was passed at the rate of 3-4 liters/hour (ozone concentration 6%) for 16 hours into a solution of 10 g cyclic ketone (IXa) in 45 ml dry chloroform. The solution of ozonide was then run into 20 ml water and stirred for 34 hours at a temperature of 60-65°. The acids were neutralized with sodium carbonate (11.5 g). The neutral products were extracted with ether. Removal of the ether left 2.2 g viscous, dark-brown liquid. The water was driven off from the solution of salts in vacuum and the salts were treated with 25 ml concentrated hydrochloric acid. The organic acids were extracted with ether and dried with sodium sulfate.

Distillation of the acids gave 1.1 g formic acid (b.p. 100-102°) and 5.1 g higher acids with b.p. 100-125° (4 mm). Redistillation of these acids gave a fraction of 1.8 g with b.p. 120-125° (4 mm) from which, after lengthy standing (1-1.5 months) separated 0.4 g crystalline α-deutero-α-isopropyl-β,β-dimethyllevulinic acid (X) with m.p. 48° [6].

Oxidation of the monodeutero-ketoacid (X) with bromide lye. Into a solution of 0.66 g NaOH in 7 ml water was introduced 0.34 g acid (X), and dropwise addition was then made of 1.04 g bromine with continuous stirring and cooling with iced water. After the bromine had been added, stirring was continued at room temperature for 3.5 hours. The bromoform was extracted with ether. The water was distilled off from the solution of salts in vacuum; the salts were decomposed with 20 ml concentrated hydrochloric acid. The organic acids were extracted with ether and dried with sodium sulfate. After removal of the ether, the residue was recrystallized from hot water. Yield 202 mg α-deutero-α-isopropyl-β,β-dimethylsuccinic acid (XI) with m.p. 134-135° [6].

The water obtained on combustion of this acid had an excess denisty of 3880 γ; recalculation for one introduced hydrogen gives a value of 3880 · 16 = 62,100 γ. Consequently, nearly the whole of the deuterium had remained in the molecule of acid (XI). This, convincingly, shows the correctness of the ionic mechanism of cyclization of dienone (VIII) advanced in the theoretical part of this paper.

SUMMARY

1. Under the action of deuterophosphoric acid the dienone (VIII) cyclizes to the monodeutero-cyclopentenone (IXa) which, on ozonization, gives the deutero-ketoacid (X); oxidation of the latter with bromide lye leads to the deutero-dicarboxylic acid (XI).

2. The dienone (VIII) and the cyclic ketone (IX) practically do not exchange their hydrogens for deuterium in the conditions of cyclization and, consequently, the entry of deuterium into the molecule of the cyclic ketone only takes place in the instant of its cyclization.

3. The results obtained are convincing evidence of the correctness of the proposed ionic mechanism of this cyclization reaction.

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DETERMINATION OF THE COMPOSITION OF THE INDIVIDUAL HYDROCARBONS OF GASOLINES BY THE COMBINATION METHOD

COMMUNICATION 5. GASOLINE FROM EMBA PETROLEUM

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In this communication we submit the results of an investigation of the individual hydrocarbon composition of a gasoline with an end boiling point of 150° from the low-sulfur Emba petroleum of the Koschagyl deposit from hole No. 6 of the 1949 strike. The investigation was carried out by the previously described combination method [1], used for examination of two gasolines from petroleums from the Kazanbulaksky deposit [2], two Suransk gasolines [3] and a gasoline from a Tatmazinskoil [4]. As in the case of the gasolines from the Kazanbulaksky and Talmazinsk oils, the gasoline investigated in the present research was obtained by fractional distillation in the laboratory.

As a result of the investigation, the composition of the gasoline from Emba oil was accounted for to the extent of 81.1%. It was found to contain in all 50 hydrocarbons, which were determined quantitatively. Their distribution by classes is set forth in Table 1.

TABLE 1

Distribution by Classes of the Hydrocarbons Found

Class of hydrocarbon	No. hydrocarbons in gasoline
Paraffins	22
Cyclopentanes	9
Cyclohexanes	13
Aromatics	6
	50

In the further discussion the gasoline from Emba oil will, for brevity, be called TsE-1. The system for designation of the fractions by letters is the same as in the previous investigations [1-4]. All the individual hydrocarbons found in the gasoline are calculated in percentages by weight of the whole gasoline and set forth in Table 2. The same table gives the total material balance of the whole investigation. The data of Table 2 permit the establishment of the group composition of the gasoline, taking into account the individual paraffins with normal and branched structures, as well as the individual cyclopentane and cyclohexane hydrocarbons. This is illustrated in Table 3.

As we see from Tables 2 and 3 (Table 2 on next page), the gasoline from Emba petroleum is predominantly naphthenic (56.1%). The ratio between the amounts of cyclopentanic and cyclohexanic hydrocarbons is 0.48.

Only 21.8% of the paraffinic hydrocarbons out of the total amount of paraffins have a normal structure and these are mainly lower molecular paraffins (C_3, C_4, C_5, and C_6). Of the isoparaffins present, 88% possess a tertiary carbon atom and 12% a quaternary carbon atom. Consequently hydrocarbons with a tertiary carbon atom predominate among the branched-chain paraffins. The greater proportion (approx. 75%) of all the isoparaffins with tertiary carbon atoms have only one side chain, while the remainder each have two side chains.

TABLE 3

Group Composition of Gasoline TsE-1

Hydrocarbons	Content in weight % of the gasoline
Normal paraffins	4.8
Paraffins with a tertiary carbon atom	15.3
Paraffins with a quaternary carbon atom	2.1
Cyclopentanes	18.3
Cyclohexanes	37.8
Aromatics	2.8

TABLE 2

Individual Hydrocarbons Found in Gasoline TsE-1

Hydrocarbon	Content, in wt-% of the TsE-1	Hydrocarbon	Content, in wt-% of the TsE-1
Paraffin hydrocarbons			
Propane	0.18	2,2-Dimethylpentane	0.66
n-Butane	1.75	2,3-Dimethylpentane	1.99
Isobutane	1.28	2,4-Dimethylpentane	0.33
n-Pentane	1.77	3,3-Dimethylpentane	0.60
2-Methylbutane	3.55	n-Octane	0.43
Neopentane	0.13	3-Methylheptane	1.07
n-Hexane	0.70	4-Methylheptane	0.54
2-Methylpentane	1.77	2,2-Dimethylhexane	0.15
3-Methylpentane	1.27	2,4-Dimethylhexane	0.59
2,2-Dimethylbutane	0.55	3-Methyloctane	0.82
2,3-Dimethylbutane	0.96	4-Methyloctane	1.10
		Total	22.2
Cyclopentane hydrocarbons			
Cyclopentane	0.32	cis-1,3-Dimethylcyclopentane	1.59
Methylcyclopentane	3.51	trans-1,3-Dimethylcyclopentane	1.99
Ethylcyclopentane	0.99	1,2,3-Trimethylcyclopentane	2.52
1,1-Dimethylcyclopentane	0.88	1,2,4-Trimethylcyclopentane	4.10
Trans-1,2-dimethylcyclopentane	2.39	Total	18.3
Cyclohexane hydrocarbons			
Cyclohexane	4.64	1-Methyl-2-ethylcyclohexane	0.39
Methylcyclohexane	13.06	1-Methyl-3-ethylcyclohexane	0.58
Ethylcyclohexane	1.89	1-Methyl-4-ethylcyclohexane	0.58
1,1-Dimethylcyclohexane	0.98	1,1,3-Trimethylcyclohexane	3.39
1,2-Dimethylcyclohexane	2.27	1,2,4-Trimethylcyclchexane	0.97
1,3-Dimethylcyclohexane	6.19	1,3,5-Trimethylcyclohexane	0.58
1,4-Dimethylcyclohexane	2.27	Total	37.8
Aromatic hydrocarbons			
Benzene	0.04	Other cyclohexane hydrocarbons of the composition C_9H_{18} (not identified)	(0.78)
Toluene	0.54	Remained unidentified	81.1
Ethylbenzene	0.12	Sulfur compounds and losses	7.58
o-Xylene	0.54		0.96
m-Xylene	1.18	Losses	7.94
p-Xylene	0.42	Residues in flask during fractionation	2.38
Total	2.8	Total in % of the TsE-1	100.0

Inspection of the composition of the paraffins by groups of hydrocarbons with identical molecular weight shows that all the possible isomers of C_5 and C_6 hyrocarbons are found in the gasoline. Of the C_7 hydrocarbons in this gasoline, only all the possible dimethylpentanes are present. The C_8 hydrocarbons found are n-octane (although in very small amount – 0.43%) and two methylheptanes (2-methylheptane not found). Of the isooctanes with two side chains, only two isomers were found: 2,2- and 2,4-dimethylhexanes. Highly branched isooctanes are completely absent from

TsE-1. Of the C_9 hydrocarbons, two representatives are found: 2- and 3-methyloctanes. Consequently, with increasing molecular weight the number of different isomers of hydrocarbons of the paraffin series and the total content of paraffinic hydrocarbons of identical molecular weight decrease.

The cyclopentane content of the gasoline is insignificant. Among the cyclopentanic hydrocarbons with one side chain, methylcyclopentane predominates. Of the cyclopentanic hydrocarbons with two side chains present in the gasoline, apart from cis-1,2-dimethylcyclopentane, all the possible dimethylcyclopentanes are represented, including 1,1-dimethylcyclopentane. It should be pointed out that, as seen in Table 2, among the dimethylcyclopentanes, the trans-forms in all cases predominate over the cis-forms. In addition to dimethylcyclopentanes, TsE-1 gasoline contains a considerable amount of trimethylcyclopentanes. With increasing molecular weight of the cyclopentanic hydrocarbons, their content in TsE-1 gasoline rises.

The content of cyclohexanic hydrocarbons in TsE-1 gasoline is double that of the cyclopentanic hydrocarbons (37.8% against 18.3%). A noteworthy feature is the relatively high content of methylcyclohexane (13.06%) in comparison with the other representatives of the hydrocarbons of this class. The most plentiful representative of the cyclohexanes with two methyl groups in the gasoline is 1,3-dimethylcyclohexane; 1,2- and 1,4-dimethylcyclohexanes are present in identical amounts. Among the methylethylcyclohexanes the hydrocarbons with side chains in the 1,3-position again predominate. Among the trimethylcyclohexanes 1,1,3-trimethylcyclohexane with a quaternary carbon atom predominates. The percentage content of cyclohexanic hydrocarbons rises insignificantly with increasing molecular weight.

The aromatics content of TsE-1 gasoline (2.8%) is very low in comparison with the other classes of hydrocarbons. The content of individual aromatic hydrocarbons falls off in the following order: m-xylene, toluene, o-xylene, p-xylene, ethylbenzene and benzene. Here, as in the case of cyclohexanic hydrocarbons, there is a noteworthy predominance of hydrocarbons with one side chain or with two side chains in the meta-position. Furthermore, as in the case of cyclopentanic hydrocarbons, a sharp rise is observed in the percentage content of aromatic hydrocarbons with rising molecular weight.

EXPERIMENTAL

Preparation of a broad cut of ShE-1 and its fractionation. The oil in copper stills was distilled off to give a ShE-1 fraction with an end boiling point of 200°. The evolved hydrocarbon gases were collected in traps cooled to −70°, and at the conclusion of the fractionation they were added to the distillate. The resultant ShE-1 fraction had the following characteristics: n_D^{20} 1.4245, d_4^{20} 0.7579, aniline point 61.3°, sulfur content 0.024* weight-%.

The results of fractionation of the broad cut in a column with an efficiency of 25 theoretical plates are set forth in Table 4 and Fig. 1. The AE-1 fraction had the following characteristics: n_D^{20} 1.4170; d_4^{20} 0.7561; aniline point 48.2°, sulfur content 0.0106 weight-%. Subsequently, all the calculations of content of individual hydrocarbons and fractions obtained at separate stages of the investigation were carried out on the complete TsE-1 gasoline, comprising fractions K_1, L and A, i.e. all fractions boiling up to 150°. This TsE-1 fraction weighted 1392.2 g.

TABLE 4

Results of Fractionation of ShE-1 Gasoline

Fraction	Boiling limits in °C (760 mm)	Weight in g	Content of fraction in weight-%	
			on ShE-1	on TsE-1
Taken for distillation	–	2005	100.0	
Gaseous portion K_1E-1	–	59	2.94	4.24
Light fraction LE-1	21.8 - 54.9	89	4.44	6.39
Main fraction AE-1	54.9 -150.1	1244	62.04	89.355
Residue	Above 150.1	594	29.63	–
Losses	–	19	0.95	–

Examination of gases and light fraction (K_1 and L). The gaseous portion K_1E-1 and the light fraction LE-1 contained sulfur compounds. For the purpose of eliminating the readily volatile sulfur compounds, the ampoule containing the gaseous fraction K_1E-1 was connected to a train of absorbers comprising a sodium hydroxide washer, a bubbler containing sulfuric acid, a silica gel column and spiral tube traps cooled with liquid air. The gases were slowly passed through this system and condensed in the spiral traps. Nitrogen was passed through the system to purge

* The sulfur content was determined by the method of combustion in a lamp.

out the gaseous hydrocarbons. After weighing the ampoule and the spiral traps before and after the experiment, the ampoule containing fraction L, which had been heated to +30° toward the end of the experiment, was connected to the same system. The gas liberated in this way was collected in the same traps together with the gas from the gaseous fraction K_1, and was likewise purged from the system with nitrogen. The combined lots of purified gas were designated by the letter K_1', while the combined non-evaporated residues were designated by L'. Results of experiments on purification of the bases of fractions K_1 and L from sulfur compounds are set forth in Table 5.

TABLE 5

Results of Purification of K_1E-1 Gases from Sulfur Compounds

Fractions	Weight in g			Content of fractions, in weight-%	
	K_1E-1	LE-1	Total	On K_1 L	On TsE-1
Taken for purification	59.2	89.0	148.2	100.0	10.63
Gas $K_1'E$-1	50.5	0.70	51.2	34.55	3.67
Light fraction L'E-1	7.04	86.83	93.8	63.29	6.73
Sulfur compounds and losses	1.70	1.50	3.2	2.16	0.23

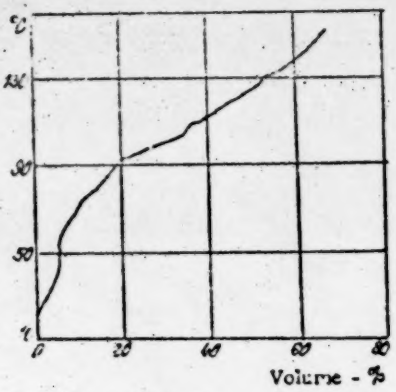

Fig. 1. Curve of fractionation of K_1E-1

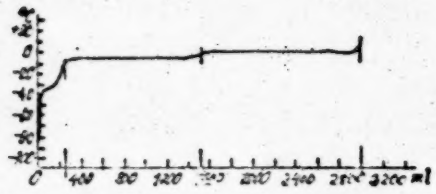

Fig. 2. Curve of fractionation of KE-1 in a Podbielniak column

Fractionation of the purified gas K' was carried out in a Podbielniak column. Results of the fractionation are set forth in Table 6 and in Fig. 2.

TABLE 6

Results of Fractionation of K'E-1 Gas

Hydrocarbon	Weight in g	Content of hydrocarbons in weight-%	
		on $K_1'E$-1	α_1 TsE-1
Taken for fractionation	8.68	100.0	3.67
Propane	0.429	4.94	0.18
Isobutane	3.036	34.93	1.28
n-Butane	3.448	39.72	1.46
Neopentane	0.058	0.67	0.02$_5$
Residue with b.p. above + 16°	1.35	15.55	0.57
Losses	0.36	4.15	0.15

The residue after fractionation of the gas with b.p. above +16° was not combined with the light cut L' due to its small amount (as specified in the scheme [1]); its quantitative composition was evaluated on the basis of the refractive index of n_D^{20} 1.3541; it contained in weight-%:

	On residue	On TsE-1
Isopentane	88.85	0.51
n-Pentane	11.15	0.06

The light cut L'E-1 of the gasoline likewise contained sulfur compounds. The latter were removed by chromatographic adsorption. The fraction was passed at a temperature of −10 to −45° through an adsorption column filled with silica gel and was eluted first with ethanol and then with water. Results of these experiments are set forth in Table 7.

Distillation of the gas (debutanization) from the desulfurized light cut was carried out again in a Podbielniak column. Results of the fractionation are set forth in Table 8.

Examination of debutanized fraction ME-1. Fraction ME-1 was fractionated in a column with an efficiency of 40 theoretical plates. The fractionation curve (Fig. 3) was plotted simultaneously with the collection of the cuts.

TABLE 7

Results of Adsorptive Separation of Sulfur Compounds from Light Fraction L'E-1

Fraction	Weight in g	Content of fraction, in weight-%	
		on fraction L'E-1	on TsE-1
L'E-1 passed through	36.05	100.0	6.73
Desulfurized light fraction L_1'E-1	35.16	97.53	6.56
Sulfur compounds and losses	0.89	2.47	0.17

TABLE 8

Results of Debutanization and Fractionation of Desulfurized Light Fraction L_1'E-1

Hydrocarbon	Weight in g	Content of hydrocarbons, in weight-%	
		on L_1'E-1	on TsE-1
Taken for fractionation	33.15	100.0	6.56
n-Butane	1.56	4.44	0.29
Neopentane	0.54	1.54	0.10
Debutanized light cut	32.50	92.46	6.07
Losses	0.55	1.56	0.10

The amount of fractions and their properties are set forth in Table 9. The constants of fraction I are seen to correspond perfectly to those of pure 2-methylbutane (b.p. 27.85°; n_D^{20} 1.3537 and d_4^{20} 0.6197) while the constants of fraction II are close to those of pure n-pentane (b.p. 36.07°, n_D^{20} 1.3575, d_4^{20} 0.6262). Consequently the amounts of fractions obtained represent the contents of these hydrocarbons in the gasoline.

The residue of fraction ME-1, as shown by an examination of the Ramen spectrum, has the following composition:

Content, in weight-%

	On residue	On TsE-1
2,2-Dimethylbutane	40	0.43
Cyclopentane	30	0.32
2-Methylpentane	20	0.21
n-Pentane	10	0.11.

Separation of aromatic hydrocarbons from the mixture of paraffins and naphthenes in main fraction AE-1. Fraction AE-1 was subjected to chromatographic adsorptive resolution into the aromatic BE-1 fraction and the paraffin-naphthenic fraction VE-1. Since the aromatic content of fraction A is low (6%), the adsorptive resolution was carried out with isolation of an intermediate fraction. Complete resolution was achieved by a fresh chromatographic adsorption of the intermediate fraction using pentane as the displacement liquid. Results of the separation are set forth in Table 10.

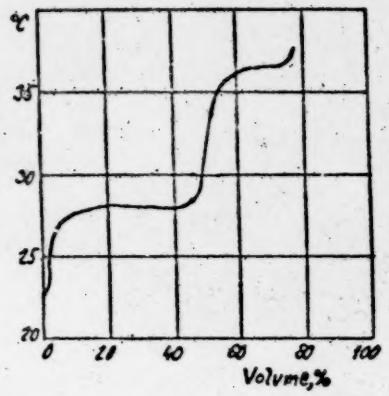

Fig. 3. Curve of fractionation of ME-1

TABLE 9

Results of Fractionation of the Light Cut ME-1

Boiling range in °C (760 mm)	Weight in g	n_D^{20}	d_4^{20}	Aniline pt. in °C	Content of fraction in weight-%	
					on ME-1	on TsE-1
Taken for fractionation	31.6	–	–	–	100.0	6.07
20.0-32.0	15.8	1.3540	0.6190	76.8	50.00	3.04
32.0-37.7	8.3	1.3574	0.6252	71.1	26.27	1.60
Residue	5.5	1.3792	0.6732	59.7	17.56	1.07
Losses	1.9				6.17	0.37

Table 10 gives both the actual amounts of fractions isolated and the corrected amounts; the latter were obtained by adding to the actual amount those amounts of the fractions which were used up in carrying out qualitative reactions for aromatic hydrocarbons and for determination of the refractive index.

The dearomatized fraction V did not contain sulfur. Aromatic fraction B contained about 0.02% sulfur, representing approximately 7% of all the sulfur present in the original gasoline A.

TABLE 10
Chromatographic Resolution of Fraction AE-1

Amount of fraction AE-1 taken in g	Results of resolution										
	aromatics BE-1				paraffin-naphthene portion VE-1				losses		
	actual in g	corrected in g	% on the AE-1	% on TsE-1	actual in g	corrected, in g	% on the AE-1	% on TsE-1	in g	% on the AE-1	% on the TsE-1
1146.3	42.9	43.3	3.8	3.37	1095.1	1095.77	95.6	85.41	7.3	0.63	0.56

The isolated fractions had the following constants and analyses:

	n_D^{20}	d_4^{20}	Aniline pt., in °C	Sulfur content, in wt-%
BE-1	1.4902	0.8536	—	~0.02
CE-1	1.4154	0.7505	51.2	0

Examination of aromatics of CE-1. The aromatic hydrocarbons of BE-1 were fractionated in a column with an efficiency of approx. 40 theoretical plates. At the same time a fractionation curve was plotted and fractions were collected which corresponded to benzene, toluene and xylenes. The xylene fraction (III) was investigated with the help of Raman spectra. Results of fractionations, properties of fractions and results of optical analysis are set forth in Table 11. With the aim of driving off the whole of the xylene fraction, pure decalin was added toward the end of the distillation.

TABLE 11
Results of Fractionation of the Aromatics of BE-1

Fraction	Boiling range, in °C (760 mm)	Weight of fraction, in grams	n_D^{20}	d_4^{20}	Content of fraction, in wt-%	
					on BE-1	on TsE-1
	Taken for fractionation	38.6	1.4902	0.8536	100.00	3.37
I	89.2-103.7	0.45	1.4543	0.7811	1.17	0.04
II	103.7-127.9	6.1	1.4768	0.8312	15.80	0.54
III	127.9-150.0	28.2	1.4941	0.8607	73.06	2.46
	Residue	1.4			3.63	0.12
	Losses	2.45			6.35	0.21

It is seen from the data that the physical properties of fraction I identify it with benzene, while those of fraction II correspond to toluene. We may therefore assume that the amounts of these two fractions correspond to the content of benzene and toluene in the gasoline.

Results of optical analysis of fraction III

	Content of hydrocarbon, in weight-%	
	On fraction III	On TsE-1
o-Xylene	22	0.54
m-Xylene	46	1.18
p-Xylene	17	0.42
Ethylbenzene	5	0.12
Not identified	8	0.20

The presence of sulfur compounds in the aromatic fractions interfered with the sharpness of the fractionation and was reflected in the constants found for the hydrocarbons.

Dehydrogenation of the cyclohexanic hydrocarbons. The paraffin-naphthenic fraction V was subjected to dehydrogenation for conversion of the cyclohexane hydrocarbons into aromatics. Fraction V was passed over an iron-platinum catalyst at 300° at a velocity of 0.8-1.0 liters/liter· hour continuously for 24 hours. The results obtained are set forth in Table 12.

TABLE 12

Dehydrogenation of the Paraffin-Naphthenic Fraction VE-1

Fraction	Amount of fraction VE-1 taken, in g	Fraction GE-1 obtained				Hydrogen and losses		
		actual, in g	corrected, in g	in wt.% on VE-1	in wt.% on TsE 1	in g	in % of VE-1	in % of TsE-1
BE-1	748.0	704.4	704.4	94.17	80.43	43.6	5.83	4.98

In this table the corrected amounts of catalyzate G wereobtained by adding to the actual amounts of G those amounts of the latter which had been used up in determining the refractive index. The losses include the hydrogen liberated on dehydrogenation of the hexamethylenes whose amount was not determined.

The physical properties of the original fraction V and of the catalyzate G obtained after dehydrogenation are as follows:

	n_D^{20}	d_4^{20}	Aniline point, °C
VE-1	1.4152	0.7505	51.2
GE-1	1.4413	0.7840	+15.4

The physical properties of the catalyzate indicate that gasoline from Emba petroleum contains a considerable amount of cyclohexanic hydrocarbons.

Resolution of catalyzate GE-1 into aromatics and a mixture of paraffins and cyclopentanes. Catalyzate GE 1 was subjected to chromatographic adsorptive resolution into an aromatic fraction DE-1 (resulting from dehydrogenation of the cyclohexanic hydrocarbons) and a paraffin-cyclopentanic fraction ES-1. Catalyzate GE-1, which contained approx. 40% aromatic hydrocarbons (this was determined on a separate sample), was directly eluted with isopentane without isolation of an intermediate fraction. Results of resolution of catalyzate GE-1 are set forth in Table 13.

TABLE 13

Chromatographic Resolution of Catalyzate GE-1

Amount taken of catalyzate GE-1, in g	Results of Resolution										
	Aromatics DE-1				Paraffin-cyclopentanic portion EE-1				Losses		
	actual, in g	corrected, in g	in % of GE-1	in % of TsE-1	actual, in g	corrected, in g	in % of GE-1	in % of TsE-1	in g	in % of GE-1	in % of TsE-1
539.7	216.8	221.3	41.00	32.98	301.2	301.2	55.81	44.89	17.20	3.19	2.57

After the isopentane had been driven off the isolated fractions DE-1 and EE-1 had the following constants:

	n_D^{20}	d_4^{20}	Aniline point, °C
DE-1	1.4966	0.8659	--
EE-1	1.4073	0.7352	57.9

Investigation of Aromatics D. The aromatic hydrocarbons DE-1, obtained by dehydrogenation of the cyclohexanic hydrocarbons, were fractionated in a column with an efficiency of about 40 theoretical plates (in a similar manner as for aromatics B). Results of the fractionation, properties of the fractions and results of optical analysis are set forth in Table 14. The table also includes the results of recalculation of the amounts of isolated aromatic fractions to the corresponding amounts of cyclohexanic hydrocarbons present in the original gasoline.

Investigation of the paraffin-cyclopentanic fraction EE-1. The paraffin-cyclohexanic fraction EE-1 was freed from isopentane and fractionated in a column with an efficiency of 50 theoretical plates into narrow cuts. Previously with the same column a curve was plotted of the fractionation of 100 ml EE-1 fraction with continuous collection of distillate with a reflux number of 45-50. The fractionation curve of EE-1 is shown in Fig. 4. The vertical strokes designate the limits of subsequent taking-off of narrow cuts whose selection was governed by the character of the fractionation curve and by the boiling points of the individual hydrocarbons.

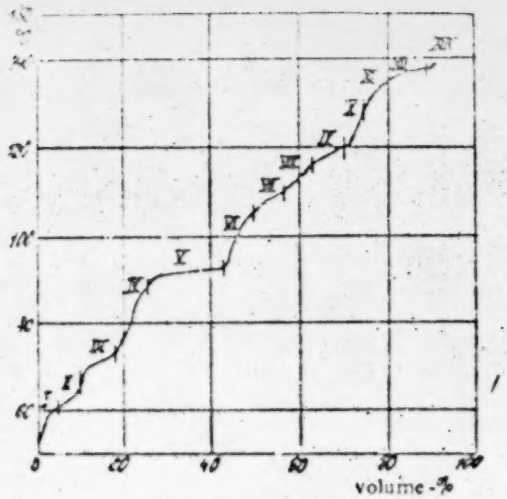

Fig. 4. Curve of fractionation of EE-1

After the fractionation curve had been plotted 300 ml of fraction EE-1 was fractionated into narrow cuts in the same column with continuous take-off of distillate and with a reflux number of 40-45. In all 13 narrow cuts were collected. Results of the fractionation of the paraffin-cyclopentanic fraction E into narrow cuts are set forth in Tables 15 and 16 together with the properties of the obtained cuts and the data of a Raman spectroscopic investigation of the cuts. The data for optical analysis of the cuts are in accord with their physical properties.

Table 2 presents all the data, in percentages by weight of TsE-1 gasoline, on the composition of the individual hydrocarbons it contains, as determined in the course of the present research. The overall results of the study are also adduced in the same table.

Laboratory assistants T.V.Lapshina, V.A.Ovodova, K.G. Ryabova and G.S.Taits participated in this research

TABLE 14

Results of Fractionation of Aromatics DE-1

Fractions	Boiling range, in ° C (760 mm)	Weight of fraction, in grams	n_D^{20}	d_4^{20}	Content of fraction, in wt-% of DE-1	Content of corresponding cyclohexanes, in wt-% of TsE-1
	Taken for fractionation	61.1	1.4966	0.8659	100.00	
I	78.4-100.0	7.5	1.4971	0.8712	12.27	4.36
II	100.0-128.0	22.0	1.4953	0.8641	36.01	12.64
III	128.0-150.0	22.15	1.4970	0.8655	36.25	12.63
IV	150.0-173.5	6.85	1.4960	0.8695	11.21	3.59
	Residue	0.45			0.74	0.25
	losses	2.15			3.52	1.23
					Total	35.00

Aromatic hydrocarbons	Content, as weight-% of fraction III	Cyclohexanic hydrocarbons	Content, as wt-% of TsE-1
(1)	(2)	(3)	(4)
Results of optical analysis of fraction III			
o-Xylene	18	1,2-Dimethylcyclohexane	2.27
m-Xylene	49	1,3-Dimethylcyclohexane	6.19
p-Xylene	18	1,4-Dimethylcyclohexane	2.28
Ethylbenzene	15	Ethylcyclohexane	1.89

TABLE 14 (cont.)

(1)	(2)	(3)	(4)
Results of optical analysis of fraction IV			
1-Methyl-2 ethylbenzene	10	1-Methyl-2-ethylcyclohexane	0.39
1-Methyl-3 ethylbenzene	15	1-Methyl-3-ethylcyclohexane	0.58
1-Methyl-4 ethylbenzene	15	1-Methyl-4-ethylbenzene	0.58
1,2,4-Trimethylbenzene	25	1,2,4-Trimethylcyclohexane	0.97
1,3,5-Trimethylbenzene	15	1,3,5-Trimethylcyclohexane	0.58
Unidentified	20		0.79

TABLE 15

Results of Fractionation of the Paraffin-cyclopentanic Fraction EE-1

Fractions	Boiling range in °C (760 mm)	Weight of fraction in grams	Content of fraction in weight-%		n_D^{20}	d_4^{20}	Aniline point in °C
			of EE-1	of FtE-1			
	Taken for fractionation of E	220.5	100.0	44.89	1.4073	0.7352	57.9
I	48.2-62.0	11.8	5.35	2.40	1.3749	0.6617	70.1
II	62.0-67.8	7.8	3.54	1.59	1.3762	0.6638	69.0
III	67.8-74.0	20.3	9.21	4.13	1.4021	0.7296	41.1
IV	74.0-89.0	13.5	6.12	2.75	1.3985	0.7161	57.9
V	89.0-92.5	39.1	17.73	7.96	1.4040	0.7296	54.3
VI	92.5-105.0	13.9	6.30	2.83	1.4098	0.7412	52.9
VII	105.0-110.0	15.1	6.85	3.07	1.4082	0.7374	62.1
VIII	110.0-116.5	13.7	6.21	2.79	1.4095	0.7385	62.3
IX	116.5-120.0	17.6	7.98	3.58	1.4122	0.7409	60.5
X	120.0-128.5	10.7	4.85	2.18	1.4180	0.7567	57.3
XI	128.5-135.0	8.2	3.72	1.67	1.4175	0.7549	62.7
XII	135.0-138.0	23.7	10.75	4.83	1.4215	0.7626	61.4
XIII	138.0-144.3	13.5	6.12	2.75	1.4182	0.7022	64.8
	Residue	9.9	4.49	2.01			
	Losses	1.7	0.77	0.35			
			99.99	44.89	—	—	—

SUMMARY

1. Gasoline with an end boiling point of 150°, obtained from low-sulfur Emba petroleum (Koschagyl), was analyzed with the help of the combination method of investigation of the individual hydrocarbons of straight-run gasolines.

TABLE 16

Results of Optical Investigation of the Narrow Cuts of the Paraffin-Cyclopentanic Fraction EE-1

Hydrocarbons found by the optical method	Content of hydrocarbons in wt-% of fraction	Content of hydrocarbons in wt-% of TsE-1
Fraction I		
2,2-Dimethylbutane	5	0.12
2,3-Dimethylbutane	40	0.96
2-Methylpentane	55	1.32
Fraction II		
2-Methylpentane	15	0.24
3-Methylpentane	80	1.27
n-Hexane	5	0.08
Fraction III		
n-Hexane	15	0.62
Methylcyclopentane	85	3.51
Fraction IV		
2,2-Dimethylpentane	24	0.66
2,4-Dimethylpentane	~12	0.33
Cyclohexane	~10	0.28
3,3-Dimethylpentane	22	0.60
1,1-Dimethylcyclopentane	32	0.88
Fraction V		
2,3-Dimethylpentane	25	1.99
cis-1,3-Dimethylcyclopentane	20	1.59
trans-1,3-Dimethylcyclopentane	25	1.99
trans-1,2-Dimethylcyclopentane	30	2.39
Fraction VI		
Methylcyclohexane	~15	0.42
Ethylcyclopentane	35	0.99
1,2,4-Trimethylcyclopentane	30	1.42
Fraction VII		
2,2-Dimethylhexane	~5	0.15
2,4-Dimethylhexane	10	0.31
1,2,4-Trimethylcyclopentane	60	1.84
1,2,3-Trimethylcyclopentane	~25	0.77
Fraction VIII		
1,2,4-Trimethylcyclopentane	30	0.84
2,4-Dimethylhexane	~10	0.28
1,2,3-Trimethylcyclopentane	~50	1.39
Not identified	~10	0.28
Fraction IX		
4-Methylheptane	15	0.54
3-Methylheptane	30	1.07
1,1-Dimethylcyclohexane	15	0.54
1,2,3-Trimethylcyclopentane	10	0.36
Not identified	30	1.07
Fraction X		
1,1-Dimethylcyclohexane	20	0.44
n-Octane	20	0.43
Not identified	60	1.31
Fraction XI		
1,1,3-Trimethylcyclohexane	25	0.42
Not identified	75	1.25
Fraction XII		
1,1,3-Trimethylcyclohexane	50	2.42
Not identified	50	2.41
Fraction XIII		
1,1,3-Trimethylcyclohexane	20	0.55
3-Methyloctane	30	0.82
4-Methyloctane	40	1.10
Not identified	10	0.28

2. The individual hydrocarbon composition of gasoline from Emba petroleum was established to the extent of 81.1 weight-% of the total gasoline. Total losses were approx. 8%.

3. It was found that the investigated gasoline from Emba petroleum was naphthenic. Among the paraffinic hydrocarbons the branched-chain compounds predominate. Among the cyclopentanic hydrocarbons the chief representative is methylcyclopentane, and a series of hydrocarbons is present with two and three side chains. The cyclohexanic hydrocarbons present in largest quantity are methylcyclohexane, 1,3-dimethylcyclohexane and 1,1,3-trimethylcyclohexane. m-Xylene predominates among the aromatic hydrocarbons.

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SYNTHESIS AND CATALYTIC HYDROGENOLYSIS OF 1,1,2-TRIMETHYLCYCLOPROPANE

B. A. Kazansky, M. Yu. Lukina and V. A. Ovodova

Continuing our study of the behavior of hydrocarbons of the cyclopropane and cyclobutane series in the conditions of catalytic hydrogenolysis over platinized carbon, we subjected 1,1,2-trimethylcyclopropane to hydrogenolysis.

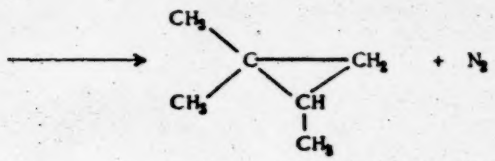
It was found that the three-membered 1,1,2-trimethylcyclopropane ring is completely ruptured by a single pass of the hydrocarbon at a space velocity of 0.4 through a tube containing platinized carbon at a temperature of 60°, the sole product of hydrogenolysis being 2,2-dimethylbutane.

For this investigation we synthesized a large quantity of 1,1,2-trimethylcyclopropane; it is usually prepared by debromination of 2-methyl-2,4-dibromopentane; it was so obtained by Zelinsky and Tselikov [1], Ostling [2], Whitmore and Carney [3], Shortridge and Boord [4], Levina and Gladshtein [5], Bartleson and co-workers [6], and finally in 1952 by Kelso, Greenlee, Derfer and Boord [7]. In the last-mentioned research the synthesis was performed on the large scale and approx. 4 liters of reaction product was fractionated in a column with an efficiency of 135 theoretical plates; it was then found to contain, apart from 1,1,2-trimethylcyclopropane, 2-methylpentane and 2-methylpentenes with the double bond in different positions. The yield of hydrocarbon mixture in this investigation was 60-85%, and about 70% of the mixture consisted of 1,1,2-trimethylcyclopropane.

1,1,2-Trimethylcyclopropane may also be synthesized by Kizhner's method [8]:

mesityl oxide

3,5,5-trimethylpyrazoline



1,1,2-trimethylcyclopropane

This reaction, which gave a good yield of pure 1,1,2-trimethylcyclopropane, was bound up with experimental difficulties since the decomposition temperature of 3,5,5-trimethylpyrazoline (approx. 220°) is above its boiling point (160°). Due to this circumstance the decomposition of the pyrazoline must be carried out in sealed tubes by heating not more than 5 ml of substance for 7-8 hours at 230°.

A recent paper by Petrov [9] gives a short account of the synthesis of 1,1,2-trimethylcyclopropane by the Kizhner reaction whereby the pyrazoline base is decomposed at atmospheric pressure in a catalytic furnace in a flow system in presence of KOH and platinized porcelain at 300°. The author points out that the product of decomposition consists of a mixture of hydrocarbon and undecomposed trimethylpyrazoline which was separated by fractionation. The yield of hydrocarbon is not stated.

We decided to prepare 1,1,2-trimethylcyclopropane by the Kizhner method but without application of pressure using the method proposed by Huang-Minlon [10] for decomposition of alkylidene hydrazines. This method consists in refluxing a mixture of the carbonyl compound, 85% hydrazine hydrate solution, caustic alkali and triethylene glycol at a temperature of 180-220° in a flask. By introducing a few changes into this procedure and using commercial mesityl oxide, from which 3,5,5-trimethylpyrazoline is easily formed, we were able to effect complete decomposition

in eight hours. The yield of hydrocarbon with constant boiling point was 41.7% of the theoretical, reckoned on the pyrazoline base.

Table 1 lists the constants of 1,1,2-trimethylcyclopropane obtained in the above-cited researches and in the present work.

TABLE 1

Authors	B.p. in °C (p in mm mercury)	n_D^{20}	d_4^{20}
Zelinsky and Tselikov [1]	56-57 (750)	1.3848	0.6822
Orling [2]	59-60 (760)	1.3896	0.6888
Whitmore and Carney [3]	56.5-57.0 (760)	1.3880	0.6967
Ditto [3]	55.5-56.5 (760)	1.3876	0.6941
Lankelma and co-workers [6]	51.7-52.7 (735)	1.3850	0.6853
Levina and Gladshtein [5]	52.0-52.3 (760)	1.3845	0.6861
Kizhner [8]	52.8 (756)	1.3866	0.6949
Kelso, Greenlee, Derfer and Board [7]	52.55 (760)	1.3864	0.6947
Petrov [9]	53.0	1.3872	0.6927
Present research	52.6 (760)	1.3862	0.6948

EXPERIMENTAL

Preparation of 3,5,5-trimethylpyrazoline. The pyrazoline base was prepared by distilling commercial mesityl oxide (b.p. 127-129°) and an 85% solution of hydrazine hydrate. In a round-bottomed flask fitted with a reflux condenser was placed 96.6 g (3 moles) hydrazine hydrate, and 98.1 g (1 mole) mesityl oxide was slowly run in with stirring. Considerable heat was developed. To the cooled reaction mass was added solid NaOH and the mixture separated into layers. The aqueous layer was removed, the base was dried with solid NaOH, and the unreacted hydrazine hydrate was distilled off; the 3,5,5-trimethylpyrazoline was then distilled from a Favorsky flask to give 70-80 g base boiling at 158-160°. The yield of distilled 3,5,5-trimethylpyrazoline was 60-70% of the theoretical.

Preparation of 1,1,2-trimethylcyclopropane. The synthesis was carried out in a round-bottomed liter flask fitted with a thermometer reaching to the bottom and a glass-packed 30 cm column. The receiver was connected to a spiral trap cooled to −70°. In the flask were placed 78.4 g (1.4 moles) solid KOH, 500 ml triethylene glycol (technical with b.p. 165°/14 mm) and 44.8 g (0.4 mole) distilled pyrazoline base. The mass was gently heated over a burner to drive off a little water (temperature of vapor 100°). When the temperature inside the flask had reached 210°, a sand bath was put underneath and the heating continued. Reaction commenced at 220-235° and the vapor temperature then dropped to 60-70° and hydrocarbon began to come off. The reflux take-off was so adjusted that the vapor temperature was at a minimum and it was continued until the temperature started to rise sharply—this usually occurred when the temperature of the reaction mass was 255-260°. The distillate from the receiver and the trap was diluted with iced water before separating off the hydrocarbon layer. It was washed twice with cooled, dilute hydrochloric acid, water, sodium carbonate solution and again with iced water. The dried hydrocarbon was distilled over metallic sodium in a glass-packed column with an efficiency of 30 theoretical plates to give 14.1 g hydrocarbon boiling at 52.6° (760 mm). The average yield from many experiments was 41.7% of the theoretical reckoned on the 3,5,5-trimethylpyrazoline. Characteristics of the hydrocarbon: d_4^{20} 0.6948; n_D^{20} 1.3862. Found MR 28.43; Calculated for C_6H_{12} MR 27.71; increment of MR 0.72; aniline point of 1,1,2-trimethylcyclopropane 48.3°.

Hydrogenolysis of 1,1,2-trimethylcyclopropane. The catalyst in the form of 10 ml (3.2 g) platinized carbon was charged into a catalysis tube with a diameter of 10 mm, heated in a tubular electric furnace fitted with a resistance of the Heraeus type. The temperature was measured with a chrome-Alumel thermocouple; the hydrocarbon was introduced into the tube through a piston apparatus for uniform proportioning of liquid [11]. The speed of introduction of hydrogen was adjusted so that the volume of gas coming off from the reactor was 1 liter per hour. The catalyzate was collected in a receiver fitted with a trap; the receiver was immersed in a mixture of dry ice and acetone. The catalyst was stabilized by passing through cyclopentane in a hydrogen stream at 300°; after 3 hours the activity of the catalyst for formation of n-pentane was found to be constant. All the subsequent experiments were carried out over this specimen of catalyst. The constants of the paraffinic hydrocarbons which can be obtained by hydrogenolysis of 1,1,2-trimethylcyclopropane are set forth in Table 2.

Results of the experiments are set forth in Table 3.

TABLE 2

Hydrocarbon	B.p. (°C) at 760 mm	n_D^{20}	d_4^{20}
2,2-Dimethylbutane [12]	49.741	1.36876	0.64916
2,3-Dimethylbutane [12]	57.988	1.37495	0.66164
2-Methylpentane [12]	60.271	1.37145	0.65315

TABLE 3

Temp. of exp. in (°C)	Space velocity	n_D^{20} of catalyzate	d_4^{20}
100	0.4	1.3688	0.6492
100	0.4	1.3684	—
60	0.4	1.3684	0.6489
60	0.4	1.3687	—
26	0.4	1.3862	—

TABLE 4

Fraction	B.p. in °C at 760 mm	Volume of fraction	n_D^{20}	d_4^{20}
I	49.6-49.8	1.0	1.3687	0.6491
II	49.8	13.0	1.3687	0.6489
III	49.8-80.0	1.0	—	—

The catalyzate from the first four experiments in amount of 16 ml was fractionated in a column containing metallic packing with an efficiency of 30 theoretical plates. 6 ml n-heptane was also introduced into the column. Results of the fractionation are set forth in Table 4.

It is clear from these data that catalytic hydrogenation of 1,1,2-trimethylcyclopropane brings about complete rupture of the three-membered ring even at 60° with formation of 2,2-dimethylbutane.

SUMMARY

1. 1,1,2-Trimethylcyclopropane was synthesized in 41.7% yield by decomposition of 3,5,5-trimethylpyrazoline by Kizhner's procedure except that no pressure was applied.

2. It was established that 1,1,2-trimethylcyclopropane in presence of platinized carbon and hydrogen is completely cleaved at 60° with formation of 2,2-dimethylbutane.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 12. HYDROCONDENSATION OF CARBON MONOXIDE WITH 1-HEXENE

Ya. T. Eidus, N. I. Ershov and E. M. Terentyeva

The catalytic hydrocondensation of carbon monoxide with olefins has been carried out with α-olefins of the aliphatic series containing not more than four carbon atoms in the molecule [1]. Attempts to extend this reaction to tri- and tetra-substituted ethylenes – trimethylethylene and tetramethylethylene – showed [2] that these hydrocarbons only enter to the extent of 5-10% into the reaction of hydrocondensation with carbon monoxide, and are hydrogenated to the extent of 30-50% to isopentane and 2,3-dimethylbutane, respectively. Cyclohexene, which can be regarded as a disubstituted ethylenic hydrocarbon, was only methylated to the extent of 7-10% when we used it in this reaction [3], being transformed into mono- and 1,2-dimethyl- derivatives, while it also partly entered into irreversible catalytic and hydrogenation reactions. It was a matter of interest to establish the reason for the small extent to which cyclohexene entered into the reaction: was it due to the higher molecular weight of this hydrocarbon in comparison with C_3 to C_4 olefins, or to the fact that it is not an α-olefin but a symmetrically disubstituted ethylene? With this objective in the present investigation we have studied the behavior in hydrocondensation with carbon monoxide of 1-hexene, a monosubstituted ethylenic hydrocarbon with a molecular weight differing very slightly from that of cyclohexene.

EXPERIMENTAL

The apparatus and the procedure for the experiments remained the same as in the previous studies [1]. The starting 1-hexene was synthesized by two methods. The first (and simpler) one consisted in dehydration of 1-hexanol (b.p. 156-157°; d_4^{20} 0.8193; n_D^{20} 1.4131) over alumina in a flow system at 350°, with a space velocity of 0.3-0.5 liters/liter/hour in a weak nitrogen stream [4]. After prolonged drying over anhydrous calcium chloride, the hexene was distilled in a column, packed with single metal spirals, with an efficiency of 40 theoretical plates. The 61-66° (754 mm) fraction was again dried for a long period over anhydrous copper sulfate and refractionated in the column. The 63-63.8° (753 mm) fraction was collected; it had d_4^{20} 0.6733; n_D^{20} 1.3882; Found MR 29.50; Calculated for C_6H_{12} MR 29.44. Literature data [5,6]: b.p. 63.7; 63.5° (760 mm), d_4^{20} 0.6733; 0.6747; n_D^{20} 1.3880; 1.3886. About 160 ml 1-hexene was obtained by this method and was used in experiments 226 and 226a. The 1-hexene used in experiments 227 and 228 (amount about 200 ml) was obtained by a second, more complicated, method giving a purer product, free from isomers (2-hexene, 3-hexene, etc.). This second method consisted in the thermal decomposition of hexyl acetate by the method of Van Pelt and Wibaut [7]. In the first step of this synthesis, 1-hexanol is acetylated with a mixture of acetic anhydride, b.p. 137-140° (758 mm), and 10% acetyl chloride, b.p. 50-51° (758 mm) to give hexyl acetate (b.p. 166-171°) in a yield of up to 90% reckoned on the original 1-hexanol. In the second step of the synthesis the acetic ester is decomposed at 460-490° over glass wool in a nitrogen stream at a flow velocity of the ester of 8 drops per minute. The crude reaction product was separated from the acid layer, washed with weak sodium bicarbonate solution and with water, dried over calcined potassium carbonate and distilled from a Favorsky flask. The following 3 fractions were collected:

Fraction I., b.p. up to 75°, yield 77.8%.
Fraction II., b.p. 75-157°, yield 13.7%.
Fraction III., b.p. 157-170°, yield 8.5%.

Fraction I was treated as follows for removal of hexanol from the hexene: It was shaken several times in a separating funnel with concentrated $CaCl_2$ solution, washed with water, dried for a long time over anhydrous $CaCl_2$ and refluxed in a flask over metallic sodium for 2 hours; it was then distilled in a column to 64.5°. The hexene obtained in this way was again distilled in the same column and a fraction was collected in a yield of approx. 50% reckoned on the original 1-hexanol; this fraction had a constant boiling point of 62.7° (743 mm); it had d_4^{20} 0.6734; n_D^{20} 1.3882; Found MR 29.50; Calculated for C_6H_{12} MR 29.44; bromine number found (Kaufmann method) 190.8; calculated 190.7. Fig. 1 shows the curve of fractionation of hexene in the column.

The original 1-hexene was introduced into the glass catalytic tube (diameter 10 mm) from an automatic buret. The experiments were performed at atmospheric pressure and a temperature of 190° in a flow system. The products were collected in two receivers at room temperature and at −80° respectively. The samples of catalyst used were from a single batch.

The experimental data and their evaluation

1. 1-Hexene (without a carrier gas). Apart from investigating the behavior of 1-hexene in hydrocondensation with carbon monoxide, we carried out experiments with 1-hexene along and with a binary mixture of C_6H_{12} and H_2 in similar conditions. Results obtained in an experiment with 1-hexene are set forth in Table 1 (experiment 226a).

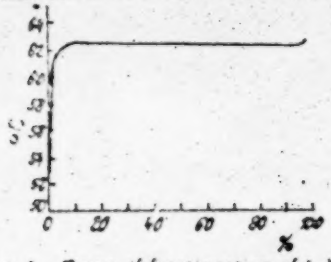

Fig. 1. Curve of fractionation of 1-hexene

Over catalyst 54 (after experiment 228, described below, had been carried out over it, followed by regeneration and purging with nitrogen) was passed 1-hexene for 5 hours with a space velocity of 0.4 liter/liter/hour. From 79 ml hydrocarbon introduced was obtained 75.8 ml (95.9%) liquid catalyzate with the constants d_4^{20} 0.6735 and n_D^{20} 1.3888, only deviating slightly from the constants of the original 1-hexene (see Table 1). Distillation of 60 ml catalyzate from a Favorsky flask resulted in the whole coming over at 62.5-64° (748 mm), indicating recovery of substantially the whole of the original 1-hexene. Nor were any gaseous reaction products obtained.

TABLE 1

Experiment 226-a

Expt. No.	Catalyst No.	Duration of experiment, in hours	Amount of 1-hexene (moles) passed through	Space velocity in liters/liter/hour			Liquid catalyzate obtained		Contraction of gas in %
				of hexene	of original gas	of C_6H_{12} + gas	in ml	in volume % of original hexene	
226a	54 (regen)	5.0	0.63	0.40	—	92.0	75.8	95.9	—
226	53	8.0	0.47	0.24	101	145	51.9	88.0	61.7
227	53	11.5	0.80	0.29	34	86	92.0	92.0	83.0
228	(regen.) 54	5.0	0.47	0.40	73	144	55.5	92.5	60.0

2. 1-Hexene in a hydrogen stream. Experiment 226 (Table 1) was carried out with 1-hexene in a stream of hydrogen over freshly prepared catalyst 53 (weight of catalyst 20 g, length of layer 40 cm). Hexene was passed through for 8 hours with a space velocity of 0.24 liter/liter/hour. The ratio by volume of 1-hexene to hydrogen in the gas phase was 1 : 3. The contraction of the gas was 61.7%. On the basis of analysis in a Podbielniak column (5.2 liters HTD taken for analysis) and of gas analysis of the separate fractions, the final gas had the composition by volume 86.3% H_2, 7.0% CH_4, 6% C_2H_6, 0.5% C_2H_4 and 0.2 % C_3H_8. The original hydrogen reacted to the extent of 67.2%. The hydrocarbon gases present in the final gas were products of decomposition of the original hexene and amounted to 3.1 mole-% of the hexene passed through.

From 59 ml starting hexene was obtained 51.9 ml (88%) liquid catalyzate. Heating of the latter to 21° caused 250 ml gas to come off, this gas condensed completely at −80° and had the composition: 13.3% ethylene, 4.4% ethane, 46.7% butylenes and 35.6% butane. Quantitatively this gas represents 1.3 mole-% of the starting hexene. Consequently the gaseous products of hydrogenolysis made up 4.6 % of the total.

After debutanization and drying over anhydrous copper sulfate the catalyzate had d_4^{20} 0.6608; n_D^{20} 1.3786; bromine number 27.0. 42 ml of catalyzate was fractionated in a column with an efficiency of 30 theoretical plates at a pressure of 751 mm. The fractionation curve is shown in Fig. 2.

In Table 2 are detailed the individual cuts, their content by volume in the catalyzate, values of d_4^{20} and n_D^{20}, bromine number and content of unsaturated hydrocarbons.

We see from Fig. 2 and Table 2 that between the limits of 21.0-62.0° about 8.6% (by volume) catalyzate distilled off, between the limits 62.0-69.0° 80% came off. The residue, which was distilled off from a 10 ml Favorsky flask, boiled at 70-150° and represented 8.4% of the catalyzate. Fractions II-IV (Table 2) with a boiling

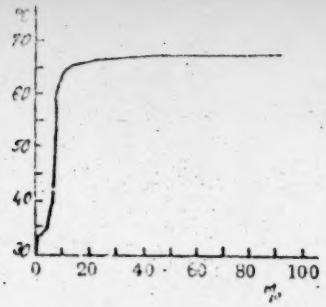

Fig. 2. Curve of fractionation of catalyzate of experiment 226.

range of 33.5-38.5° consisted mainly of n-pentane with a trace of pentene. The largest of these, fraction II, had d_4^{20} 0.6280 n_D^{20} 1.3588, which were very close to the constants of n-pentane [6]: b.p. 36.0°; d_4^{20} 0.6264; n_D^{20} 1.3577. Consequently the liquid product of hydrogenolysis of hexene had a saturated character, which can be explained by the large excess of hydrogen in the original gas. The main bulk of the catalyzate (over 80%) was in fractions VI-IX. As we see from the constants and bromine numbers, these fractions consisted to the extent of 80-90% of hexane (b.p. 68.7°; d_4^{20} 0.6594; n_D^{20} 1.3750 [5]) and to the extent of 10-20% of hexene. On the basis of the data obtained, the starting 1-hexene entered into the reaction to the extent of 84.5% and hydrogenation to hexane took place to the extent of 61.3% (by weight) on the starting 1-hexene and to the extent of 70.8% on the reacted 1-hexene. Higher boiling products accounted for 7.6 and 9.0% respectively, and lower boiling products for 11.7 and 13.7% respectively.

3. 1-Hexene in a mixed stream of carbon monoxide and hydrogen. Two experiments, numbers 227 and 228 (Table 1), were performed with passage of 1-hexene in a stream of a gaseous mixture of carbon monoxide and hydrogen. Experiment 227 was carried out with catalyst 53 after its regeneration, and experiment 228 with catalyst 54 (weight of catalyst 15.5 g, length of layer 40 cm) which had previously been used for 5 hours in the hydrocondensation of carbon monoxide with ethylene.

TABLE 2

Experiment 226

Fractions	Boiling range, in °C	Content, in vol-% of original catalyzate	d_4^{20}	n_D^{20}	Bromine number	Amount of unsaturated hydrocarbons, in %	C_n
I	21.0-33.5	0.5	—	—	—	—	C_5
II	33.5-35.5	3.6	0.6280	1.3588	—		C_5
III	35.5-36.0	0.9	—	1.3605	—		C_5
IV	36.0-38.5	0.5	—	—	—		C_5
V	38.5-41.0	0.7	—	—	—		
VI	41.0-62.0	2.4	—	1.3672	—		
VII	62.0-65.5	6.0	0.6590	1.3780	38.1	20	C_6
VIII	65.5-66.5	6.2	0.6602	1.3790	31.4	17	C_6
IX	66.5-67.5	67.5	0.6593	1.3770	18.9	10	C_6
X •							
Residue	(70.0-150)	8.4	0.6846	1.3902	10.4		> C_6
Losses		3.3					
Original catalyzate		100	0.6608 ••	1.3786••	27.0••		

• Less than 0.1 ml came over in the range of 67.6-70.0°.

•• The constants relate to the original catalyzate after taking off fraction I.

Experiment 227. 1-Hexene was passed through for 11.5 hours with a space velocity of 0.29 liters/liter/hour. The space velocity of the gas mixture (11.6 CO; 88.4 H_2) was 34 liters/liter/hour. The composition of the gas phase was 61.0% C_6H_{12}, 4.6% CO, 34.4% H_2. The over-all space velocity (gas and vapor phases) was 86 liters/

liter/hour. The contraction of the $H_2 - CO$ gas mixture was 83.0%. Composition of final gas: 2.1% CO_2; 54.0% H_2; 7.1% CO; 12.1% $C_4H_8 + C_3H_6$; 1.4% C_2H_4 and 23.0% C_nH_{2n+2}. On the basis of analysis in the Podbielniak apparatus the $C_5 : C_7 : C_6 : C_4$ ratio in the final gas was roughly 12 : 6 : 1 : 12. The starting hydrogen had reacted to the extent of 89.5%, the CO to the extent of 89.8%.

From 100 ml of hexene passed through was obtained 92.0 ml (92%) liquid catalyzate with the constants (after drying over anhydrous copper sulfate): d_4^{20} 0.6753; n_D^{20} 1.3902; bromine number 157. Heating of the dried catalyzate to 28° caused separation of 0.6 ml condensate in the receiver cooled to −80°. Of this 0.6 ml, about 0.4 ml readily changed to gas (about 100 ml) at room temperature. The residue (0.2 ml) had n_D^{28} 1.3750.

The debutanized catalyzate (74 ml) was fractionated in a column with an efficiency of 30 theoretical plates at a pressure of 738 mm. The fractionation curve is shown in Fig. 3.

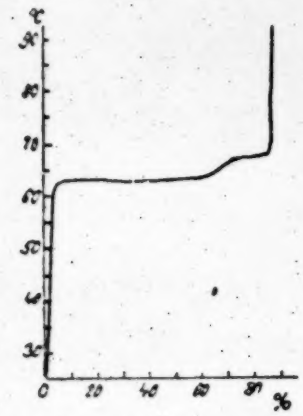

Fig. 3. Curve of fractionation of catalyzate of experiment 227.

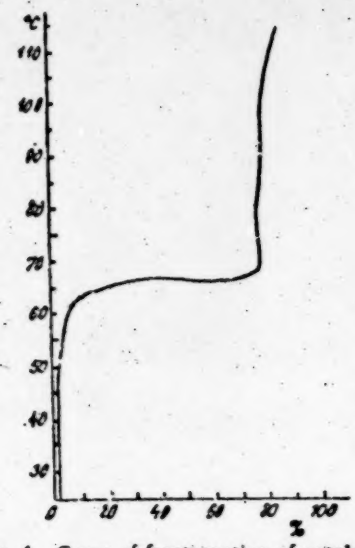

Fig. 4. Curve of fractionation of catalyzate of experiment 228.

In Table 3 are detailed the individual fractions and their constants. As we see from Fig. 3 and Table 3, in the range 28.0-62.5°, 5.4% (by volume) of catalyzate came over; in the range 62.5-70.5° 82% distilled. The residue, which was distilled from a 15 ml Favorsky flask, boiled in the range of 70.5-155° and represented 11.4% of the catalyzate. On the basis of its properties, fraction I was a mixture of pentane and pentene with slight preponderance of the latter; fractions III and IV comprising in all 55.6% of the catalyzate, consisted of nearly pure (95.4-99.6%) 1-hexene. Fractions V and VI comprised a mixture of hexene and hexane in the ratio of 1.7 : 1 and 1 : 1.5 respectively.

The data show that in experiment 227 the 1-hexene reacted to the extent of 35.9%. The total yield of hexane was 12.4% (by weight) on the starting and 34.6% on the reacted 1-hexene. The less intense hydrogenation than in experiment 226 may be explained by the lower content of hydrogen in the starting gas. Moreover in experiment 227 the higher boiling products amounted to 13.7% of the starting and 38.2% of the reacted 1-hexene, i.e., more than in experiment 226, which was carried out in the absence of carbon monoxide in the gas phase.

Experiment 228 was conducted with catalyst 54 whose activity had previously been characterized, in a hydrocondensation reaction using 54.8% C_2H_4, 6.8% CO and 38.4% H_2, by a yield of liquid condensate of 554.8 ml/m^3 at a space velocity of the starting gas of 109 liters/liter/hour. After the experiments on hydrocondensation of carbon monoxide with ethylene, hydrogen was passed over the catalyst at 450° for 3 hours; experiment 228 was then started. 1-Hexene was passed through for 5 hours with a space velocity of 0.40 liters/liter/hour. Space velocity of gas mixture (13.6 CO : 86.4 H_2) 73 liters/liter/hour. The composition of the gas-vapor phase was 49.5% C_6H_{12}, 7.0% CO and 43.5% H_2. The over-all space velocity (gas-vapor phase) was 144 liters/liter/hour. Composition of final gas: 1.9% CO_2; 79.8% H_2; 13.7% CO; 0.4% C_4H_8; 4.2% C_3H_6; 0.0% C_nH_{2n+2}. The starting hydrogen reacted to the extent of 63.1%, the carbon monoxide to the extent of 60%. The contraction of the original gas was 60% (Table 1).

TABLE 3

Experiment 227

Fractions	Boiling range, in °C	Content, in vol-% of original catalyzate	d_4^{20}	n_D^{20}	Bromine number	Amount of unsaturated hydrocarbons, in %	C_n
I	28.0-41.0	2.7	0.6386	1.3700	116.3	52	C_5
II	41.0-62.5	2.7	0.6675	1.3858	119.4	63	$C_5 + C_6$
III	62.5-62.6	38.1	0.6721	1.3878	189.7	99.6	C_6
IV	62.6-63.5	17.5	0.6751	1.3875	181.7	95.4	C_6
V	63.5-67.5	17.0	0.6688	1.3865	116.9	62.4	C_6
VI	67.5	9.7	0.6673	1.3850	73.5	39	C_6
VII*	92.5-155.0	11.4	0.7193	1.4110	65.9		$> C_6$
VIII							
Residue and losses		1.9	—	—			$> C_6$
Starting catalyzate		100	0.6753	1.3902	157.0		

* 1.0 ml came over at 67.6-92.5°.

TABLE 4

Experiment 228

Fractions	Boiling limits, in °C	Content, in vol-% of original catalyzate	d_4^{20}	n_D^{20}	Bromine number	Amount of unsaturated hydrocarbons in %	C_n
I	To 28	1.6	—	—	—	—	
II	28.0-62.0	7.2	0.6520	1.3810	166.7	79	C_5
III	62.0-67.4	68.2	0.6653	1.3848	129.7	68	C_6
IV*	79.5-295.0	19.6	0.7264	1.4140	49.8		$> C_6$
V		2.4	—	—	—		$> C_6$
Residue							
Losses		2.0	—	—	—		
Origina. catalyzate	28-295	100	0.6988	1.3960	109.2		

* 0.2 ml came over in the range of 67.4-79.5°.

From 60.0 ml starting 1-hexene was obtained 55.5 ml (92.5%) catalyzate, from which (after drying over anhydrous copper sulfate) was isolated, by heating to 28°, 0.8 ml volatile condensate in the receiver cooled to −80°. The liquid catalyzate then had the following properties: d_4^{20} 0.6988; n_D^{20} 1.3960; bromine number 109.2. 50 ml was fractionated in the above-mentioned column (30 theoretical plates) at a pressure of 746 mm. The fractionation curve is shown in Fig. 4. Results of fractionation are set forth in Table 4.

We see from Fig. 4 and Table 4 that in the range of 28.0-62.0° (fraction II) 7.2% (by volume) catalyzate comes over; in the range of 62.0-68.8° 68.2% (fraction III) comes over. Fraction IV, which came over nearly completely in the range of 79.5-295°, was distilled from a 25 ml Favorsky flask; it represented 19.6%, and together with fraction V 22.0% of the condensate. Fraction II, 7.2% of the total, consisted mainly of pentane and pentene with a little hexane and hexene, and contained 79% unsaturated hydrocarbons. Judging by its constants and bromine number, fraction III was a mixture of hexene and hexane in the ratio of approximately 7 : 3. Fraction IV and residue V are products of hydrocondensation of carbon monoxide with 1-hexene. These higher boiling products could not have been formed only from CO and H_2, and they were obtained with participation of the original 1-hexene. This is confirmed by the fact that if all the reacted carbon monoxide had participated only in the Orlov-Fischer-Tropsch reaction, 27 times less product could have been obtained than the total amount of fraction IV and residue V (Table 4). From the data of experiment 228 it follows that 1-hexene entered into the reaction to the extent of 58.7%, 22.6% (by weight) entered into the hydrocondensation reaction with carbon monoxide when reckoned on the original 1-hexene, and 39.8% when reckoned on the reacted 1-hexene. The hexane yield was 20.4 and 36.0% respectively.

Table 5 contains a comparison of the main results obtained in experiments 226, 227 and 228. The table shows that over freshly prepared catalyst at a somewhat low space velocity of 1-hexene (0.24 liters/liter/hour) and with excess of hydrogen in the gas phase (C_6H_{12} : H_2 = 1 : 3), i.e. in the conditions favoring hydrogenolysis and reaction of the products with 1-hexene, the latter is hydrogenated to the extent of 61.3% (by weight) to n-hexane; at the same time 7.6% was converted into higher boiling and 11.7% into lower boiling products (experiment 226).

TABLE 5

Expt. No.	Catalyst number	Catalyst	C_6H_{12} : H_2 ratio in the gas phase	Amount of CO, in %	Yield of high-boiling products, in weight-%		Yield of hexane, in weight-%	
					on starting 1-hexene	on reacting 1-hexene	on starting 1-hexene	on reacting 1-hexene
226	53	Freshly prepared	1 : 3	0.0	7.6	9.0	61.3	70.8
227	53	Regenerated	1 : 0.56	4.6	13.7	38.2	12.4	34.6
228	54	After hydrocondensation of carbon monoxide with ethylene	1 : 0.88	7.0	22.6	39.8	20.4	36.0

In presence of 4.6 % CO in the gas phase the hydrogenation to hexane proceeded to the extent of 12.4% on the starting hexene and to the extent of 34.6% on the reacted hexene. The yields of higher boiling products were respectively 13.7 and 38.2% (experiment 227). With a content of 7.0% CO in the gas phase the 1-hexene entered into hydrocondensation with carbon monoxide to the extent of 22.6%, representing 39.8% of the reacted hexene. The yield of hexane was 20.4% of the original and 36.0% of the reacted hexene (experiment 228). A similar effect of CO concentration on hydrocondensation has already been observed many times [1].

Comparison of the data obtained in this research with previous results of experiments with cyclohexene [3] show that 1-hexene enters more easily into hydrocondensation with carbon monoxide than does cyclohexene. This may be due to 1-hexene being an α-olefin whereas cyclohexene is a symmetrically disubstituted ethylenic hydrocarbon. 1-Hexene enters less readily, however, into this reaction than do the gaseous C_3-C_4 α-olefins.

SUMMARY

1. Experiments on the hydrocondensation of carbon monoxide with 1-hexene were carried out.

2. It was shown that in the usual conditions of this reaction, 22% (by weight) of the original 1-hexene enters into this reaction with formation of higher boiling hydrocarbons and about 20% of it is hydrogenated to n-hexane.

3. The yields of hydrocondensation products and of n-hexane on the reacted 1-hexene are respectively 39.8 and 36.0%.

4. The data obtained show that 1-hexene enters into the hydrocondensation reaction with carbon monoxide with greater facility than cyclohexene but less readily than gaseous C_2 — C_4 α-olefins.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 13. INFLUENCE OF THE RATIO OF ETHYLENE TO HYDROGEN IN THE ORIGINAL GAS, OF DILUTION WITH NITROGEN AND OF THE SPACE VELOCITY ON THE HYDROCONDENSATION OF CARBON MONOXIDE WITH ETHYLENE

Ya. T. Eidus, K. V. Puzitsky and I. V. Guseva

In previous communications [1, 2, 3] on the hydrocondensation of carbon monoxide with olefins, some data have already been submitted on the influence of the concentration and the ratio of the individual components in the original gas mixture upon the yield of reaction products. It was observed [1] that whereas with a composition of the starting mixture of 1 CO: $2H_2$: $3C_2H_4$ the mean yield of hydrocarbons was 343.3 ml/m^3 or 30.2 ml/liter catalyst per hour, with a composition of 1 CO: $2H_2$: 1.5 C_2H_4 the yield dropped to 195.6 ml/m^3 or 20.0 ml/liter catalyst per hour. It was shown [2] that a special part is played by the CO concentration. With rising CO content of the gas mixture in the range of 0 to 6%, the yield of gas oil steadily increases, followed by light oil and finally by heavy oil. A further fall of yield of the volatile fraction of the reaction products is offset by rise of the yield of heavier fractions, i.e., the degree of polymerization of ethylene increases. In the complete absence of carbon monoxide no polymerization at all of ethylene, propylene and butylene takes place [3]. Maximum velocity of hydrocondensation of propylene and n-butylene with carbon monoxide was observed in presence of 6 - 8% of carbon monoxide in the starting mixture. When 15-20% carbon monoxide is present in the starting gas mixture, its hydrocondensation with propylene and n-butylene is markedly inhibited in comparison with the same reaction with ethylene. The aim of the present research was to investigate the influence on the course of catalytic hydrocondensation of carbon monoxide with ethylene of the following factors: 1) volumetric ratio of ethylene and hydrogen in the starting gas mixture; 2) dilution of the whole of the starting gas mixture with an inert gas (nitrogen); 3) space velocity of the starting gas mixture.

EXPERIMENTAL

The apparatus, procedure for conducting the experiments and purification and method of analysis of the gases did not differ from those previously described [1]. The experiments were performed in a flow system at atmospheric pressure and 190°. All the catalysts used were of identical composition and prepared by the same method.

1. Influence of Volumetric Ratio of Ethylene and Hydrogen in the Starting Mixture

Experiments on the influence of the volumetric ratio of ethylene and hydrogen in the starting mixture of $C_2H_4 - H_2 - CO$ were carried out with catalyst 55 (length of layer 29 cm, volume 25 ml) with a carbon monoxide content of 3 - 6%. Duration of each experiment 5 hours. The experimental results are set forth in Table 1 and in Figs. 1 and 2.

In Table 1, the experiments are not set forth in the order of their performance (which is indicated by the number of the experiments in the first column) but in the order of rising ratio of C_2H_4/H_2 by volume in the original gas (column 4). As we see from Table 1, the content of ethylene varied in the range of 33-68%, that of hydrogen in the range of 11.7-55.2%, and their ratio by volume in the range of 0.61 - 5.81. The space velocity of the whole of the gas mixture in this series of experiments varied to an insignificant extent (94-132 liters/liter·hour). We see from Table 1 and Fig. 1 that when the C_2H_4/H_2 ratio is less than 1 and more than 4, the total yield of hydrocarbons, expressed in ml/m^3 or ml/liter·hour, is considerably lower than when $4 > C_2H_4/H_2 > 1$.

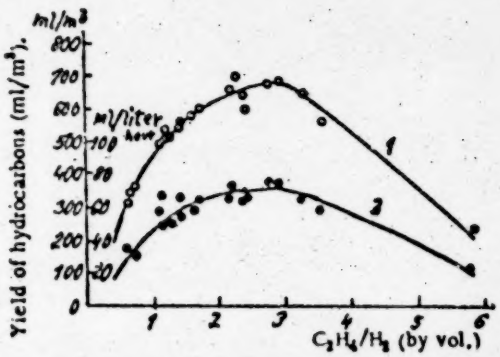

Fig. 1. Influence of ratio by volume of ethylene to hydrogen in starting mixture on yield of hydrocarbons. 1) In ml/m^3, 2) in ml/liter·hour.

TABLE 1

Experiment No.	Amount in original gas, in %		C_2H_4/H_2 ratio by volume	Space velocity in liters/liter·hr.	Contraction, in %	Yield in ml/m³				Yield of T + L + G, in ml/liter·hour	Amount of unsaturateds in gas oil, in %
	C_2H_4	H_2				of heavy oil T	of light oil L	of gas oil G	of T + L + G		
239	33.0	53.7	0.61	118	55.4	79.5	144.5	101.2	325.2	36.0	14.0
237	35.0	55.2	0.63	105	55.7	89.8	122.5	138.7	350.9	34.4	–
240	36.0	50.1	0.72	94	60.2	91.0	127.4	145.6	364.0	32.0	8.0
242	46.0	42.2	1.09	122	64.7	139.8	139.8	223.7	503.3	57.6	–
241	44.5	39.1	1.14	107	65.0	175.6	150.5	183.9	510.0	48.8	–
238	48.0	41.2	1.16	132	65.4	160.6	160.6	224.8	546.0	68.0	–
243	49.0	39.4	1.24	106	65.0	174.9	135.2	206.7	516.8	51.2	–
244	50.5	36.2	1.39	102	68.7	221.4	114.8	213.2	549.4	53.6	28.0
236	52.5	37.4	1.40	127	63.5	173.4	133.3	253.4	560.0	67.2	–
248	54.0	33.7	1.60	109	64.0	234.5	140.6	202.6	577.5	59.2	–
246	55.5	32.6	1.70	115	66.0	232.9	137.7	224.7	594.4	65.6	–
254	61.5	28.7	2.14	104	66.0	203.8	146.7	309.8	660.3	64.8	59.5
245	58.5	26.6	2.18	112	69.2	249.8	151.4	295.3	696.3	73.6	54.0
252	64.0	27.3	2.34	105	63.3	161.0	147.0	338.2	644.1	64.0	65.5
251	64.0	27.2	2.35	111	60.4	150.2	165.2	285.4	600.8	64.0	70.0
247	63.0	22.8	2.76	120	64.0	240.2	155.4	282.6	678.2	76.8	66.0
249	65.0	22.4	2.90	115	64.5	255.0	167.7	269.7	692.4	76.0	71.0
250	70.5	21.7	3.25	108	60.0	124.8	148.1	374.9	647.8	65.6	66.0
255	72.0	20.2	3.56	110	54.3	152.1	159.7	251.0	562.8	59.2	77.0
253	68.0	11.7	5.81	108	36.0	71.4	119.1	39.6	230.1	23.2	–

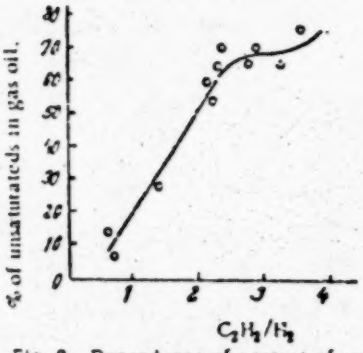

Fig. 2. Dependence of content of unsaturated hydrocarbons in gas oil upon ratio of ethylene to hydrogen in the original gas.

A maximum at a C_2H_4/H_2 ratio of 2.5–3 is observed on the plot of total yield of hydrocarbons versus C_2H_4/H_2 ratio in the starting gas. The highest yield of hydrocarbons is 700 ml/m³ or 70 ml/liter·hour. At a C_2H_4/H_2 ratio of less than 1, the total yield of hydrocarbons falls to 350 ml/m³ or 35 ml/liter·hour. At a C_2H_4/H_2 ratio greater than 4, for example at a ratio of 5.81 (experiment 253), it falls to 230 ml/m³ or 23.2 ml/liter·hour. The yield of light oil hardly changes with change of C_2H_4/H_2 ratio, whereas the yields of heavy oil and gas oil likewise pass through a maximum at a C_2H_4/H_2 ratio of 2 - 3. The rise of the C_2H_4/H_2 ratio is naturally accompanied by an increase of unsaturation of the reaction product. Thus, for example, in the gas oil the content of unsaturated hydrocarbons rises from 8-14% with a C_2H_4/H_2 ratio of 0.6 - 0.7 to 77% in the case of a C_2H_4/H_2 ratio of 3.56. The change in unsaturation of gas oil as a function of the C_2H_4/H_2 ratio is plotted in Fig. 2.

Consequently, the data show that a fall in the concentration of hydrogen to a certain limit in comparison with the mixture of $1\,CO : 2H_2 : 3C_2H_4$ brings about a rise in yield of the reaction products and an increase in their degree of unsaturation.

2. Influence of Dilution of Starting Gas Mixture with Nitrogen

Experiments in which a study was made of the effect of dilution of the original gas mixture with nitrogen were carried out over the same catalyst 55 before the latter was used for the experiments set forth in Table 1. The duration of each experiment was 5 hours. The original mixture contained 3 - 5% CO. The experimental results obtained are set forth in Table 2 and plotted in Figs. 3 and 4.

In Table 2 the experiments are set forth in the order of increasing dilution of the starting mixture with nitrogen

TABLE 2

Experiment No.	Amount in starting mixture		Ratio by volume of C_2H_4/H_2	Space velocity in liters/liter·hour	Concentration in %	Yield in ml/m³				Yield of T + L + G in ml/liter·hour
	of active gases (C_2H_4 + $+H_2$+CO)	N_2				T	L	G	T+L+G	
232	95.4	4.6	1.3	138	65.3	165.7	134.0	243.9	543.6	71.2
235	95.4	4.6	1.2	136	63.0	148.9	161.3	235.8	546.0	70.4
231	72.6	27.4	1.7	131	53.0	218.7	187.5	218.7	624.9	58.1
229	46.4	53.6	1.5	110	32.4	177.4	306.4	16.1	499.9	24.8
234	45.3	54.7	1.8	104	29.2	140.4	280.8	70.2	491.4	22.4
230	37.7	62.3	1.6	144	29.5	192.5	274.0	66.5	533.0	28.8
233	28.8	71.2	1.9	81	24.4	181.0	291.1	18.5	490.6	10.8

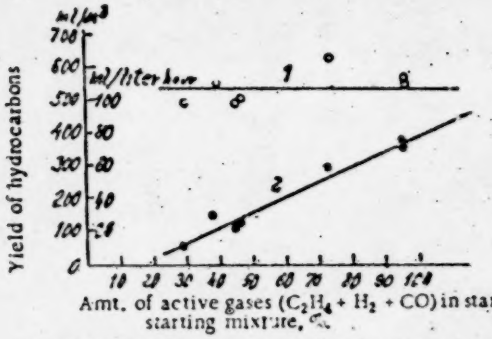

Fig. 3. Yield of hydrocarbons as a function of the dilution of the starting gas with nitrogen: 1 - in ml/m³; 2 - in ml/liter/hour.

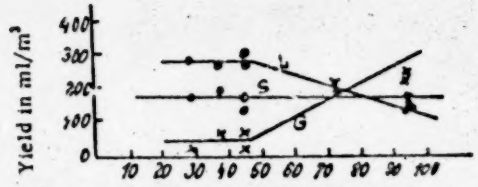

Fig. 4. Yield of various fractions of reaction products as a function of the dilution of the initial gas with nitrogen.

The enumerated values of the contraction relate to the whole of the starting mixture, while the space velocity and yields in ml/m³ relate to the active gas (C_2H_4 + H_2 + CO).

Table 2 indicates that the nitrogen content of the mixture varied between 4.6 and 71.2 %. We see from Table 1 and Fig. 3, that the total yield of hydrocarbons, expressed as ml/liter·hour, decreases linearly with dilution of the starting mixture with nitrogen. When related to 1 m³ of active gas (C_2H_4 + H_2 + CO), however, the total yield of hydrocarbons does not change appreciably with dilution and has an average value of 530 ml/m³. Similarly, as shown by Fig. 4, the yield of heavy oil in ml/m³ does not depend on the dilution and has a mean value of 180 ml/m³. The yields of light oil and gas oil (in ml/m³), however, vary sharply with dilution, the former in fact rises sharply while the second falls equally sharply with increasing content of nitrogen in the starting mixture to 55%. With further increase of the nitrogen content the yields of light oil and gas oil remain constant – the former at a mean value of 290 ml/m³ and the latter at 40 ml/m³ (Fig. 4). The observed relations are not associated with change of catalyst activity, since consecutive experiments were performed at different dilutions. This – at first sight – unexpected rise of the yield of higher molecular product (light oil) and the corresponding fall in yield of more volatile product (gas oil) may be due to the higher dilution with nitrogen increasing the portion of the surface on which nitrogen is adsorbed. It may be suggested that this portion of the surface is the least active and is characterized by a lower heat of adsorption and desorption. In the absence of nitrogen on this part of the surface the hydrocarbons formed are easily desorbed and do not attain a high molecular weight (gas oil). In the presence of a large amount of nitrogen this part of the surface is covered with nitrogen, and the consequence of this is a drop in the yield of gas oil, which is the more pronounced the greater the amount of nitrogen adsorbed. On the more active portion of the surface of the catalyst the relative concentration of CH_2 groups will be greater than in the experiments without dilution, which results in a rise in the yield of light oil. This explanation, however, calls for additional experimental confirmation.

d. Influence of Space Velocity of the Initial Gas

The space velocity may be altered by: 1) changing the linear velocity of the gas at constant volume of catalyst; or 2) changing the volume of the catalyst at constant linear velocity. We effected a change of space velocity by both methods.

a) Change of space velocity with constant volume of catalyst. These experiments were performed on catalysts 56 and 57 (each 18 g, 21 ml, layer length 26 cm). The starting mixture contained 3 - 4% carbon monoxide and 20 - 30% hydrogen. The results of the experiments are set forth in Table 3 and plotted in Fig. 5, from which we see that change of space velocity in the range of 105 - 200 liters/liter · hour does not affect the contraction of the gas, which remains at an average value of 62%, or the total yield of hydrocarbons when expressed in ml/m³, whose mean value was 680 ml/m³. With rising space velocity, however, there is a linear rise in yield, expressed in ml/liter · hour, from 64.0 at a space velocity of 105 liters/liter · hour to 131.4 at 200 liters/liter · hour.

b) Change of space velocity at constant linear velocity. These experiments were carried out with catalysts 58 and 63 (double portions of catalyst each 32 g), 59 and 62 (ordinary portions of 18 g each), 60 (1/2 portion of 9.7 g) and 61 (1/4 portion of 5 g). Results of experiments with these catalysts are set forth in Table 4 and plotted in Figs. 6 and 7.

TABLE 3

Experiment No.	Catalyst number	Duration of experiment in hours	Space velocity in liters/liter · hour	Contraction, in %	Yield, in ml/m³				Yield of T + L + G, in ml/liter · hour
					T	L	G	T + L + G	
262	57	5	200	61.4	149.9	145.0	534.9	689.8	131.4
260	57	25	186	66.9	180.3	153.6	411.9	745.8	131.0
261	57	10	177	66.6	174.1	190.4	350.3	714.8	119.5
259	56	15	170	64.3	167.2	172.6	368.8	708.6	113.0
263	57	10	161	56.9	133.1	162.5	334.3	629.9	99.5
258	56	10	155	64.7	152.9	170.6	322.9	686.4	98.6
257	56	5	143	63.0	189.2	188.2	266.2	643.6	82.7
256	56	5	105	63.3	161.0	147.0	338.2	646.2	64.0

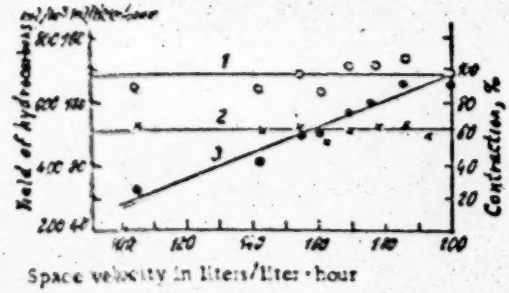

Fig. 5. Influence of space velocity of initial gas at constant catalyst volume on the yield of hydrocarbons: 1) Yield in ml/m³; 2) contraction; 3) yield in ml/liter · hour.

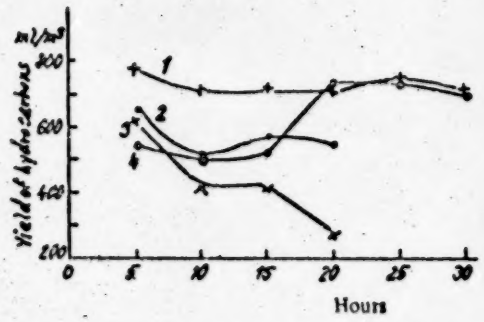

Fig. 6. Effect of duration of experiment on the dependence of the yield of hydrocarbons on the space velocity of the initial gas: 1) 186 liters/liter · hour, 1 portion; 2) 250 - 300 liters/liter · hour, 1/2 portion; 3) 500 liters/liter · hour, 1/4 portion; 4) 64 liters/liter · hour, 2 portions.

The data of Table 4 and Figs. 6 and 7 show that in experiments with 1/4 portion of catalyst (catalyst 61) at a space velocity of 500 liters/liter · hour the activity of the catalyst falls off with increasing duration of reaction. The yield of hydrocarbons falls from 623.7 to 278.7 ml/m³ or from 284 to 127 ml/liter · hour. In experiments with

TABLE 4

Experiment No.	Catalyst Number	Number of portions of catalyst	Space velocity, in liters/liter·hour	Contraction in %	Yield, in ml/m³				Yield of T+L+G, in ml/liter·hour
					T	L	G	T+L+G	
282	63	2	61	71.2	142.0	142.0	256.0	540.0	30.4
283	63	2	67	68.5	178.1	63.7	356.3	498.1	37.6
284	63	2	68	55.0	161.7	129.8	234.3	525.8	32.4
285	63	2	62	66.3	207.3	129.2	400.4	736.9	41.2
286	63	2	63	66.7	197.3	132.1	410.3	740.3	44.8
276	62	1	185	72.1	176.9	150.0	450.2	777.1	138.0
277	62	1	178	66.2	155.7	205.7	350.4	711.4	121.9
278	62	1	188	63.9	173.7	141.3	401.3	716.3	124.7
279	62	1	176	67.0	192.6	175.1	350.2	717.9	117.1
280	62	1	187	69.4	203.8	128.5	407.8	739.8	131.4
281	62	1	188	64.1	187.3	198.0	337.3	722.6	128.5
268	60	0.5	252	65.2	238.7	173.8	246.4	658.9	152.0
269	60	0.5	298	54.7	169.0	150.7	187.5	507.2	140.0
270	60	0.5	252	50.3	201.3	180.0	194.1	575.4	133.4
271	60	0.5	273	58.6	214.5	167.7	167.7	549.4	137.0
272	61	0.25	500	56.7	220.0	154.0	249.7	623.7	284.0
273	61	0.25	500	48.3	123.7	130.9	160.0	414.0	190.0
274	61	0.25	498	42.1	110.9	147.7	162.5	421.1	190.0
275	61	0.25	527	36.7	73.4	110.2	95.1	278.7	127.0

TABLE 5

Experiment No.	Catalyst Number	Number of portions of catalyst	Space velocity, in liters/liter·hour	Contraction in %	Yield, in ml/m³				Yield of T+L+G, in ml/liter·hour
					T	L	G	T+L+G	
264	58	2	64	65.6	177.4	119.3	331.5	628.2	37.3
266	59	1	124	62.6	264.6	209.0	225.0	698.6	80.0
268	60	0.5	252	65.2	238.7	173.8	246.4	658.9	152.0
272	61	0.25	500	56.7	220.0	154.0	249.7	623.7	284.0

TABLE 6

Experiment No.	Catalyst Number	Number of portions of catalyst	Space velocity in liters/liter·hour	Contraction in %	Yield in ml/m³				Yield of T+L+G in ml/liter·hour
					T	L	G	T+L+G	
267	59	1	142	64.3	195.5	158.8	231.1	585.4	76.8
257	58	1	143	63.0	189.2	188.2	266.2	643.6	82.7
265	58	2	124	61.0	153.7	167.4	381.6	702.7	84.0
266	59	1	124	62.6	264.6	209.0	225.0	696.6	80.0

1/2 and 1 portion of catalyst at space velocities of 250-300 and 186 liters/liter·hour respectively, the yield of hydrocarbons expressed in ml/m³ or ml/liter·hour remains nearly constant. In experiments with a double portion of catalyst at a space velocity of 64 liters/liter·hour, the yield of hydrocarbons expressed in ml/m³ increases with the time, whereas when expressed in ml/liter·hour (product) it remains constant.

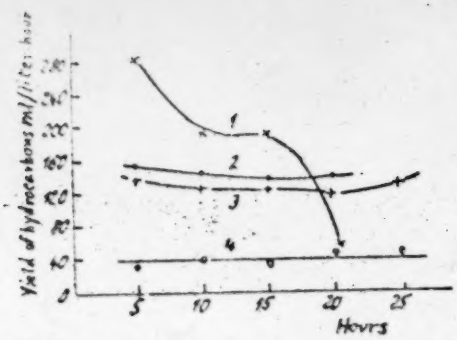

Fig. 7. Effect of duration of experiment on the dependence of the yield of hydrocarbons on the space velocity of the initial gas. 1) 500 liters/liter·hour, 1/4 portion; 2) 250-300 liters/liter·hour, 1/2 portion; 3) 186 liters/liter·hour, 1 portion, 4) 64 liters/liter·hour, 2 portions.

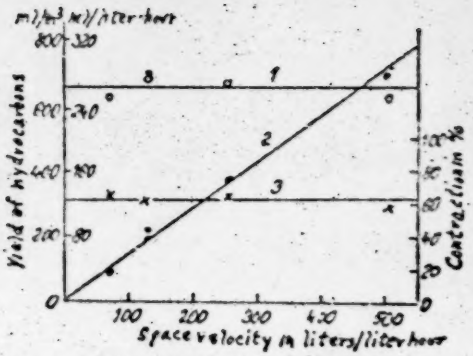

Fig. 8. Effect of space velocity of initial gas at constant linear velocity upon the yield of hydrocarbons: 1) in ml/m³; 2) in ml/liter·hour; 3) contraction.

We may note that in order to compare the results among themselves obtained at different space velocities, the first experiments in order of time in this series were taken. An exception was the double portion of catalyst (catalyst 58) with which the 25-hour experiment number 264 was carried out, and mean values after 25 hours were taken. Results of comparison of the influence of space velocity with changing volume of catalyst while maintaining constant linear velocity are set forth in Table 5 and plotted in Fig. 8.

From Table 5 and Fig. 8 we see that change of space velocity by changing the amount of catalyst has no influence upon the contraction of the gas and upon the total yield of hydrocarbons expressed in ml/m³. The total yield of hydrocarbons expressed in ml/liter·hour, however, increases linearly with the space velocity which was varied in the range of 61-500 liters/liter·hour. In Table 6 for comparison are set forth the data obtained over different catalysts (56 and 59) at one and the same space velocity (142 liters/liter·hour) with one and the same amount of catalyst (experiments 267 and 257) and with different amounts of catalyst (experiments 265 and 266). From Table 6 we see that the results are in fairly good agreement in respect to total yield, expressed as ml/m³ and as ml/liter·hour, in the experiments at one and the same space velocity.

We see from the data obtained that the method of changing the space velocity of the initial gas has little influence upon the reaction course provided that not too little catalyst is taken; too little catalyst shortens the duration of action of the catalyst and leads to a sharp drop in activity in course of time. Increase of space velocity (by either of the methods indicated) in the investigated range does not bring about a change of contraction of the gas or of the total yield of hydrocarbons in ml/m³ but leads to a linear rise of total yield when expressed as ml/liter·hour.

SUMMARY

1. An investigation was made of the influence of the ethylene/hydrogen ratio in the initial gas mixture, of dilution with nitrogen and of the space velocity upon the hydrocondensation of carbon monoxide with ethylene.

2. It was shown that the optimum ethylene/hydrogen ratio in the initial gas is 2.5-3.

3. Dilution of the initial gas mixture with nitrogen does not influence the total yield of hydrocarbons when expressed as ml/m³ but leads to a fall in yield when related to unit time and to unit volume of catalyst. Dilution of the gas with nitrogen up to a certain limit leads to rise of yield (ml/m³) of light oil and a corresponding fall of yield of gas oil.

4. Rise of space velocity in the range of 100-500 liters/liter·hour does not influence the total yield of hydrocarbons expressed as ml/m³ and leads to a linear rise of yield expressed in ml/liter·hour. When using small amounts of catalyst, the latter is quickly deactivated.

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THERMAL TRANSFORMATIONS OF 1,3-PENTADIENE

N. I. Shuikin, S. S. Novikov and T. I. Naryshkina

The study of the thermal transformations of individual hydrocarbons is of considerable interest for the understanding of industrial processes for working-up of hydrocarbon raw materials. The literature contains a large number of papers dealing with the thermal decomposition of alkanes and alkenes, whereas the transformations of alkadienes (with exception of butadiene) under the action of high temperature have hardly been studied. Thus, Kennedy and Hetzel [1] studied the reaction of dehydrocyclization of piperylene over various catalysts with the objective of obtaining cyclopentadiene; they showed that the maximum yield of this hydrocarbon is approximately 9% at 600° and a pressure of 10 - 30 mm mercury. The composition of the other products of transformation of piperylene was not studied. Frank, Emmick and Johnson [2] obtained two fractions on passing trans-piperylene at 600° through a vertical pyrex glass tube filled with glass packing:

Fraction I, b.p. 38-41.5°; yield 5%
Fraction II, b.p. 43.2°; yield 52%

The second fraction contained, apart from the original trans-piperylene, 45% of cis-piperylene.

From publications on the thermal transformations of hydrocarbons [3, 4, 5, 6] it is known that alkanes do not tend to form cyclic systems in the conditions of thermal treatment, whereas alkenes form cyclic compounds in appreciable quantity. In this research we studied the thermal transformations of 1,3-pentadiene at various temperatures in a flow system.

EXPERIMENTAL

The piperylene used in the investigation had the following characteristics: b.p. 42-42.5° (760 mm); n_D^{20} 1.4315 d_4^{20} 0.6830. Literature data: b.p. 42.4-42.6°; n_D^{20} 1.4309; d_4^{20} 0.6803 [7].

Reaction with maleic anhydride [2] enabled establishment of the ratio of stereoisomeric forms in the starting material; the latter proved to be a mixture of 53% cis- and 47% trans-isomers. The original 1,3-pentadiene was subjected to thermal treatment in a quartz tube with an internal diameter of 18 mm, heated by an electric furnace and filled with crushed quartz glass. Substitution of porcelain for the quartz did not alter the character of the pyrolytic transformations. A temperature of 600° was used; the rate of passage of the diene was 0.3 liter per liter contact material per hour. The condensate was collected in two traps arranged in series and cooled with a mixture of acetone and solid carbon dioxide.

The gaseous products of pyrolysis were analyzed in an Orsat-Lunge apparatus and by low-temperature fractionation in vacuum. The liquid products of the reaction were investigated by means of rectification, chromatographic resolution and bromination of individual fractions. The solid products of reaction (coke) were characterized by determination of their elemental composition.

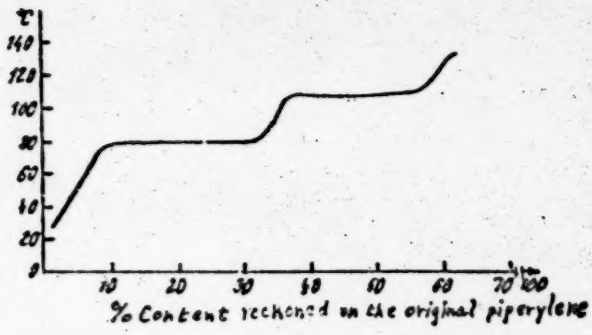

Fig. 1. Curve of fractionation of condensate from pyrolysis of piperylene.

Several preliminary experiments were carried out in which the reproducibility of the results was determined, the yields of condensates were established, and the content of cyclopentadiene and of partly sulfonatable condensate boiling up to 140° was found. The results of the experiments showed that the condensates contain up to 1% cyclopentadiene and 15% of substances

which are taken up by 80% sulfuric acid. Cyclopentadiene was determined by the colorimetric method described by Afanasyev [8]. These experiments were followed by others in which the composition of the condensates was studied in more detail. Below are set forth the data of one typical run at 600° in which from 68 g pentadiene was obtained 50 g (74% of the original) pyrolyzate with a dark-brown color. This condensate was fractionated in a column with an efficiency of 27 theoretical plates. Results of fractionation are set forth in Table 1 and plotted in Fig. 1.

TABLE 1

Results of Fractionation of Condensate Obtained by Thermal Treatment of Piperylene

Fractions	B.p.(°C)	Yield of fractions in %	n_D^{15}	Fractions	B.p.(°C)	Yield of fractions in %	n_D^{22}
I	26 - 29	–	1.3950	VIII	78 - 90	26.4	1.4995
II	29 - 34	1.4	1.4095	IX	90 - 108	2.0	1.4950
III	34 - 35	1.6	1.4025	X	108 - 110	18.0	1.4968
IV	35 - 37	0.7	1.4090	XI	110 - 135	0.8	1.4930
V	37 - 39	0.3	1.4173	XII	135 - 140	7.2	1.4958
VI	39 - 45	2.8	1.4370	Residue		36.0	–
VII	45 - 78	0.8	1.4680	Losses		2.0	–

It follows from the data of Table 1 and Fig. 1 that pentadiene is transformed into a complex mixture of hydrocarbons containing a considerable proportion of substances of high molecular weight. It is noteworthy that the pyrolyzate contains a large amount of aromatic hydrocarbons; for their identification a portion of the combined condensate from several experiments was resolved into an aromatic and an aliphatic fraction by the method of chromatographic adsorption [9]. 42.5 g condensate taken for chromatographic analysis gave 37 g (87%) aromatic hydrocarbons with n_D^{23} 1.5015, slightly contaminated with saturateds, and 4 g (10%) unsaturated hydrocarbons with n_D^{20} 1.4430. Fractionation established the absence of unsaturated hydrocarbons higher than C_5, but there was considerable contamination with aromatics. The aromatic hydrocarbons were fractionated in a column with an efficiency of 27 theoretical plates.

TABLE 2

Results of Fractionation of Aromatic Portion of Condensate from Thermal Transformations of Piperylene

Fractions	B.p.(in °C)	Yield in %	d_4^{20}	n_D^{20}	Molecular refraction MR	
					Found	Calculated
I	38-79	1.3	1.3905	–	–	–
II	79-80	34.0	1.4998	0.8782	26.17	26.31
III	80-109	2.4	1.4980	0.8665	–	–
IV	109-111	31.0	1.4962	0.8658	31.11	30.93
V	111-135	3.5	1.4940	0.8651	–	–
VI	135-136	11.3	1.4960	0.8652	35.79	35.54
VII	136-140	6.9	1.5085	0.8995	–	–
Residue		8.0	–	–		
Losses		1.6				

Results of fractionation at 760 mm are set forth in Table 2 and plotted in Fig. 2. From an inspection of the properties of the individual fractions it follows that the fraction with b.p. 79-80° consists of benzene (34%) and the 109-110° fraction consists of toluene (31.0%).

For investigation of the composition of the 135-136° fraction, 2 g of the fraction was oxidized to the corresponding acids by Ullmann's method [10]. The acids were separated and analyzed by the procedure described by Moldavsky, Kamusher and Kobylskaya [11]. Among the products of oxidation were found 0.40 g benzoic acid with m.p. 121°, 0.08 g orthophthalic acid with m.p. 190° (in sealed capillary), 0.33 g isophthalic acid and 1.10 g terephthalic acid with melting points of 63 and 138° for the respective dimethyl esters. Calculations on the basis of these results show that the 135-140° fraction contains 25% ethylbenzene, 5% o-xylene, 26% m-xylene and 44% p-xylene.

At the conclusion of the fractionation of the aromatic part of the pyrolyzate, a solid with the odor of

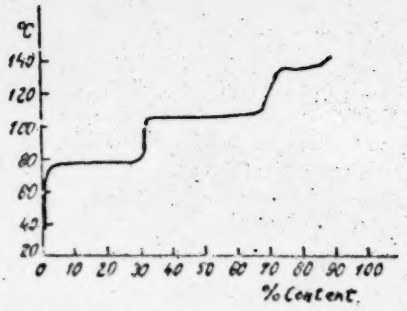

Fig. 2. Results of fractionation of aromatic portion of condensate after thermal treatment of piperylene.

naphthalene crystallized on the walls of the condenser. After recrystallization this substance (0.17 g) was dissolved in a little ethanol and poured into an alcoholic solution of an equimolar amount (0.3 g) picric acid. The resultant yellow needles were identified from the melting point (148°) as the monomolecular compound of naphthalene and picric acid. The literature [12] gives 149.5° as the m.p.

For analysis of the low-boiling portion of the pyrolyzate, the combined 29-37° fraction from several experiments (2.5 g) was brominated at 0°. The crystalline bromides (0.2 g) were separated from the liquid bromides (2.7 g). The solid tetrabromides were twice recrystallized from ethanol; they melted at 113-114°, which is the m.p. of 1,3-pentadiene tetrabromide. The liquid bromides were fractionated at reduced pressure (18 mm) to give fractions with b.p. 70-100°, 0.3 g, n_D^{20} 1.5340 (the greater portion boiled at 70-85°) and with b.p. 100-160° (predominantly 150-160°), 2.0 g, n_D^{25} 1.5880.

Analysis of fraction with b.p. 100-160°:

Found %: C 15.93; H 2.17; Br 81.9

$C_5H_8Br_4$. Calculated %: C 15.49; H 2.08; Br 82.43

On the basis of the analytical results we may conclude that the 70-100° fraction contains mainly the dibromo derivatives of C_5 alkenes while the 100-160° fraction contains isoprene tetrabromide, reported in the literature to have b.p. 157-159° (12.5-13.5 mm) [13].

Consequently, the volatile fraction of the concensate evidently contains (apart from piperylene) isoprene, pentenes and cyclopentadiene (main bulk in the 39-45° fraction)*. After passing 50 ml piperylene over the catalyst, 0.3 g coke had settled on the catalyst or the equivalent of 1% by weight of the original pentadiene. Analysis of two samples of coke (I – C 94.24% and H 5.76%; II – C 94.92% and H 5.08%) showed that it corresponds in composition to a condensed aromatic compound with the general formula $C_n H_{2n-18}$.

TABLE 3

Composition of gaseous products of thermal transformations of piperylene at various temperatures

Composition of gas	Temp. in °C		
	500	550	600
Hydrogen	27	22	23
Unsaturated C_2–C_4 hydrocarbons	3	12	23
Saturated C_1–C_4 hydrocarbons	70	66	54

It was observed that in subsequent experiments carried out in the same conditions but without regeneration of the catalyst, the yield of liquid product fell to 70-66%. This fall in yield of pyrolyzate is due to the coke deposit promoting gas formation and further coke formation. Analysis of the gas revealed that it contained 32.6% hydrogen, 54.6% saturated hydrocarbons, and 22.8% unsaturated hydrocarbons. A closer examination of the saturated portion revealed the presence of methane, ethane, propane and isobutane.

A study was also made of the influence of temperature on the character and extent of the thermal transformations of 1,3-pentadiene. For this purpose experiments were carried out with 1,3-pentadiene at 500 and 550°. The condensates were analyzed by the same methods as before. Results of analyses are set forth in Tables 3 and 4.

It follows from the data of Tables 3 and 4 that rise of temperature from 500 to 600° increases the extent of transformations of pentadiene: the amount of aromatic hydrocarbons and resins increases considerably while the content of low-boiling hydrocarbons decreases appreciably. Rise of temperature causes a significant increase in the content of unsaturated hydrocarbons in the gaseous products.

In conclusion it is necessary to mention that thermal treatment of 1,3-pentadiene in a flow system leads

* The total content of cyclopentadiene in the condensate, as indicated above, was determined in a broad cut boiling up to 140°.

TABLE 4

Composition of liquid products of thermal transformations of piperylene at various temperatures

Composition of liquid products	Temp. in °C		
	500	550	600
Unsaturated hydrocarbons with b.p. 26-39°	22	22	4
Unsaturated hydrocarbons with b.p. 39-45°	50	18	4
Aromatic hydrocarbons	15	28	54
Resin	13	32	38

to formation of a complex mixture of hydrocarbons both richer and poorer in hydrogen than the original hydrocarbon. The presence in the condensates of hydrocarbons higher in molecular weight than the original pentadiene points to the occurrence of well-marked synthesis processes in the conditions selected for the present investigation. In these conditions the process of destruction of the original hydrocarbon is probably accompanied by formation of radicals of varying complexity; recombination of some of them or their reaction with the original hydrocarbon results in formation of molecules of hydrocarbons which are readily converted into six-membered cyclic systems.

SUMMARY

1. An investigation was made of the thermal transformations of 1,3-pentadiene (piperylene) in a flow system at 600° in a quartz tube filled with crushed quartz glass.

2. In the specified conditions 1,3-pentadiene forms a complex mixture of hydrocarbons of various classes: gaseous (methane, ethane, propane, isobutane, alkenes), liquid (isoprene, pentenes, cyclopentadiene, benzene, toluene, xylenes) and solid (naphthalene, and condensed systems with the general formula C_nH_{2n-18}).

3. The yield of cyclopentadiene does not exceed 1% reckoned on the original 1,3-pentadiene.

4. Formation of a considerable amount of aromatic hydrocarbons must be attributed to condensation reactions of dienes.

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CONTACT CATALYTIC ALKYLATION OF BENZENE IN PRESENCE OF ALUMINA-SUPPORTED ZINC CHLORIDE UNDER CONDITIONS OF HIGH PRESSURE

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Insufficient attention has been given in the literature to problems of utilization of metallic halides on a solid support as alkylation catalysts. The methylation of benzene in the vapor phase was effected for the first time by Kutz and Corson [1] in presence of aluminum chloride adsorbed on activated carbon. The application of aluminum chloride as a vapor phase alkylation catalyst is mentioned in patents [2, 3]. In 1945 Schmerling and Ipatieff [4] took out a patent on the methylation of aromatic hydrocarbons in presence of zinc chloride on alumina. At 250-350°, according to the authors, the yield of toluene is 22%, and that of xylenes 25%.

Zinc chloride has been used as a catalyst for alkylation of the aromatic nucleus with alkyl chlorides and alcohols by Kuchkarev and Tsukervanik [5] who showed that condensation of benzene with n-butyl and isopropyl alcohols at 220-230° in an autoclave gives monoalkylbenzenes in a yield of 75-80% of the theoretical, calculated on the alcohol. Condensation of benzene with ethyl alcohol only takes place at 300° to form ethylbenzene in a yield of 36% of the theoretical.

In the present investigation we studied the catalytic alkylation of benzene with diethyl ether, ethylene and isopropyl alcohol in presence of alumina-supported zinc chloride. The reaction was performed in a flow system at high pressure (10 to 60 atm) and temperatures of 150-400° at various molar ratios of benzene to the alkylating agent. Alkylation of benzene with ethylene was carried out in contact with alumina and with alumina-supported zinc chloride (15 and 30% $ZnCl_2$). The experiments showed that in favorable conditions alumina does not catalyze the alkylation of benzene with ethylene. Zinc chloride supported on alumina in the amount of 15 and 30 wt-% proved an active catalyst for this reaction.

In the conditions that we established (see p. 785), the yield of broad ethylbenzene fraction with b.p. 120-140° was 16% of the theoretical reckoned on the benzene used.

In the alkylation of benzene with isopropyl alcohol the highest yields of isopropylbenzene were obtained at temperatures of 300 to 350° and pressures of 20 to 40 atm, and with a molar benzene/isopropyl alcohol ratio in the range of 4:1 to 6:1. In these conditions the yield of broad isopropylbenzene fraction (b.p. 145-160°) was 78-80% of the theoretical and that of pure isopropylbenzene (b.p. 152-153°) was 63.3% reckoned on the isopropyl alcohol taken. In the reactions which we studied, the best results were obtained by alkylation of benzene with isopropyl alcohol.

EXPERIMENTAL

Catalytic alkylation of benzene with diethyl ether, ethylene and isopropyl alcohol was carried out in a flow system. In all experiments a mixture of benzene (39 g, i.e., 0.5 mole) and alkylating agent was charged into the reactor with a space velocity of 0.45 at temperatures of 156 to 400°. The catalyzate was fractionated from a small flask with a tall Vigreux column (h = 0.5 m). In the tables are included the most typical results of the experiments. As a rule 2-3 experiments were carried out in each set of identical conditions.

Catalytic Alkylation of Benzene with Diethyl Ether

Results of the experiments on alkylation of benzene with diethyl ether are set forth in Tables 1 and 2. The influence of the benzene/diethyl ether molar ratio is plotted in curves 1 and 2 of Fig. 1. Curve 1 shows that the yield of ethylbenzene, reckoned on the ether taken, falls with increasing amount of the latter, while the yield with reference to benzene (curve 2) at first rises slowly to a maximum and then gradually falls. The benzene/ether molar ratio in the range of 4.5:1 to 6:1 may be considered the optimum.

It was established in the experiments that the most suitable conditions for alkylation of benzene with diethyl ether in contact with alumina-supported zinc chloride at high pressure are: temperature of 300 to 350°,

pressure of 20 atm, and a benzene/ether molar ratio in the range of 4.5 : 1 to 6 : 1. In these conditions the yield of broad ethylbenzene fraction with b.p. 120-140° is 13-14% of the theoretical reckoned on the benzene taken, or 74-86% reckoned on the reacted benzene.

TABLE 1

Influence of the temperature upon the catalytic alkylation of benzene with diethyl ether
(Pressure 20 atm; benzene/ether ratio = 6 : 1)

Expt. No.	Temp. in deg C.	Weight of catalyzate, in g	Results of fractionation of catalyzate (amount of fraction in g)						
			up to 85°	85-120°	120 - 140°			140-200°	Residue in g
					in g	Yield in %			
						on the benzene	on the ether		
9	250	40.0	26.0	2.5	6.2	11.5	43.5	2.3	1.5
4	300	40.5	29.0	1.5	7.0	13.2	41.2	1.0	0.5
7	350	36.0	22.0	2.5	7.5	14.1	43.0	1.5	1.6
8	400	41.0	29.0	1.5	7.0	13.2	41.2	1.0	1.0

TABLE 2

Influence of pressure on the catalytic alkylation of benzene with diethyl ether
(Temperature 300°, benzene/ether molar ratio = 6 : 1)

Expt. No.	Pressure, in atmospheres	Weight of catalyzate, in g	Results of fractionation of catalyzate (amount of fraction in g)				
			up to 85°	85-120°	120-140°	140-200°	Residue in g
4	20	40.5	29.0	1.5	7.0	1.0	0.5
12	30	37.0	20.0	2.0	7.1	2.9	4.0
13	40	37.5	20.0	1.5	6.8	3.1	4.5
14	60	38.0	21.6	2.0	6.0	4.5	5.1

Contact catalytic alkylation of benzene with ethylene

A mixture of 40% ethylene and 60% nitrogen was used for the alkylation of benzene with ethylene with the aim of reducing the yields of polyalkylbenzenes. The reaction was carried out at pressures of 20 to 40 atm and temperatures of 225 to 350° with various amounts of ethylene. Results of experiments on alkylation of benzene with the above-mentioned mixture in contact with various samples of catalysts are set forth in Table 3.

TABLE 3

Dependence of yields of alkylbenzenes on the nature of the catalyst in the alkylation of benzene with ethylene

Expt. No.	Catalyst	Temp. of expt., in deg C.	Molar ratio of benzene to ethylene	Catalyzate obtained in g	Yield of alkyl fraction in %
7	Zinc chloride on alumina (30% $ZnCl_2$)	300	1 : 1	39.0	30.7
18	Zinc chloride on alumina (15% $ZnCl_2$)	300	1 : 1	35.0	32.0
4	Alumina	300	1 : 2	35.0	none
5	Alumina	370	1 : 1	36.0	none

We see from Table 3 that alumina does not catalyze the alkylation of benzene with ethylene. Zinc chloride (15 and 30 wt-%) supported on alumina proved an active catalyst for this reaction.

In the following experiments a study was made of the influence of temperature (Table 4, experiment 7,8,9), of pressure (Table 4, experiments 6 and 11), and of the molar ratio of benzene to ethylene (Table 4, experiments 14, 15, 17) on the yield of the ethylbenzene fraction.

TABLE 4

Alkylation of benzene in contact with alumina-supported zinc chloride

Expt. No.	Temperature (°C)	Pressure, in atm.	Molar ratio of benzene to ethylene	Weight of catalyzate (in g)	Results of fractionation of catalyzate (weight of fraction in g)					
					up to 85°	85-120°	120-140°		140-200°	residue, in g
							in g	yield on benzene (in %)		
8	225	20	1 : 1	38.0	29.5	1.3	3.7	6.9	1.5	1.8
7	300	20	1 : 1	39.0	24.0	1.6	6.5	12.0	2.4	2.5
9	350	20	1 : 1	39.0	27.0	1.5	5.0	9.5	3.5	2.0
6	300	20	2 : 1	36.0	25.0	1.5	5.0	9.5	2.0	1.5
11	300	40	2 : 1	48.0	18.0	5.0	8.5	16.0	3.0	11.5
14	300	40	3 : 1	41.0	24.0	1.5	6.5	12.0	3.2	5.0
15	300	40	2 : 1	41.0	17.0	3.0	7.5	14.0	5.0	7.0
17	300	40	1 : 2	35.0	16.6	2.0	7.5	14.0	4.2	4.5
18*	300	Atmosph.	1 : 2	38.5	37.0	0.5	—	—	—	0.5

* The experiment was carried out at atmospheric pressure in a flow system.

The optimum conditions for alkylation of benzene with ethylene in contact with alumina-supported zinc chloride are: temperature 300 deg, pressure 40 atm, and molar ratio of benzene to ethylene of 2 : 1. The catalyzate obtained in these conditions contains 50% alkylbenzenes including 18.8% broad ethylbenzene fraction (b.p. 120-140°), representing 16% of the theoretical yield reckoned on the benzene taken.

The 85-120° and the 120-140° fractions from all the experiments were combined, treated with sulfuric acid to eliminate the small content of unsaturateds, washed with water, dried with calcium chloride and distilled over sodium in a column with an efficiency of 25 theoretical plates. They contained 58% ethylbenzene with b.p. 134-136°; n_D^{20} 1.4956 and d_4^{20} 0.8671, and 2% toluene with b.p. 109-112°; n_D^{20} 1.4960 and d_4^{20} 0.8670. The fractionation curve of these fractions is plotted in Fig. 2. The 109-112° fraction was oxidized by Ullmann's method to give benzoic acid which after sublimation melted at 121°. On the basis of the fractionation data the yield of pure ethylbenzene in the most successful experiment was 14.7% of the theoretical.

The combined 140-190° fractions of all the catalyzates were treated with sulfuric acid, washed with water, dried with calcium chloride and distilled over sodium in a small column. From 22 g of this broad cut was isolated a 10 g fraction with b.p. 175-186°; its constants (n_D^{20} 1.4965; d_4^{20} 0.8703) show that in the main it consists of diethylbenzenes.* Oxidation of this fraction by Ullmann's method [7] gave a mixture of phthalic acids. Separation of this mixture by the method described by Moldavsky and co-workers [8] indicated that the investigated fraction contained 15.4% o-diethylbenzene, 46.2% m-diethylbenzene and 38.1% p-diethylbenzene. The combined residues from the fractionation of the catalysts from all the experiments boiled in the range of 190-300° and was evidently a mixture of polyalkylbenzenes.

* Boiling points: o-diethylbenzene, 183.3°; m-diethylbenzene, 181.25°; p-diethylbenzene, 183.6°

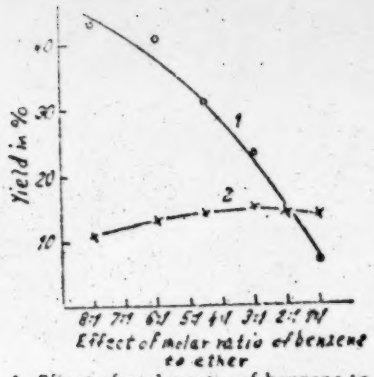

Fig. 1. Effect of molar ratio of benzene to diethyl ether on yield of the broad ethylbenzene fraction (b.p. 120-140°) at 300° and 20 atm. 1) Yield calculated on ether taken; 2) yield calculated on benzene taken.

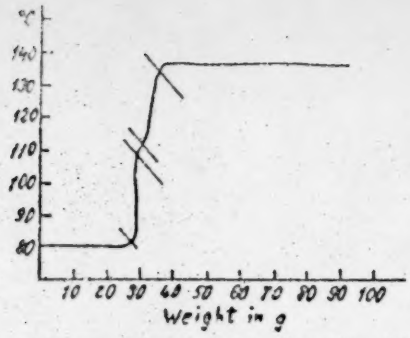

Fig. 2. Curve of fractionation of combined fractions with b.p. 85-120° and 120-140°

Alkylation of benzene with isopropyl alcohol

During alkylation with isopropyl alcohol a study was made of the influence of temperature, pressure and molar ratio of benzene to isopropyl alcohol. The influence of pressure was studied at 250° and a molar benzene/alcohol ratio of 4 : 1 (these conditions proved to be the optimum when carrying out this reaction at atmospheric pressure [9]). Results of the experiments are set forth in Table 5.

Table 5 shows that increase of pressure to above 20 atm has an insignificant effect upon this reaction; in the pressure range of 40 to 60 atm the yield of isopropylbenzene remains constant.

TABLE 5

Influence of pressure on yield of the isopropylbenzene fraction (Temperature 250°, molar ratio of benzene to alcohol = 4 : 1)

Pressure, in atm.	Weight of catalyzate, in g	Results of fractionation of catalyzate (amount of fraction in g)					
		up to 85°	85-145°	145-160°			Residue in g
				in g	Yield in %		
					on benzene	on alcohol	
10	40.0	28.0	0.5	10.0	16.6	66.6	0.3
20	40.5	27.8	0.8	10.5	17.5	70.0	0.4
40	41.0	27.5	0.5	11.0	18.3	73.3	0.5
60	40.0	26.7	0.5	11.0	18.3	73.3	1.5

The temperature effect was examined at a benzene/alcohol molar ratio of 4 : 1 and at a pressure of 40 atm (Table 6).

According to the data of Table 6 the maximum yield of isopropylbenzene is obtained at temperatures between 300 and 350°.

The influence of the molar ratio of benzene to isopropyl alcohol was studied at 300° and 20 atm. The results of these experiments are plotted in curves 1 and 2 of Fig. 3, from which we see than an increase in the amount of alcohol in the reaction mixture leads to a drop in yield of the isopropylbenzene fraction with b.p. 145-160° when reckoned on the original isopropyl alcohol, and to a rise in yield of this fraction when calculated on the benzene introduced.

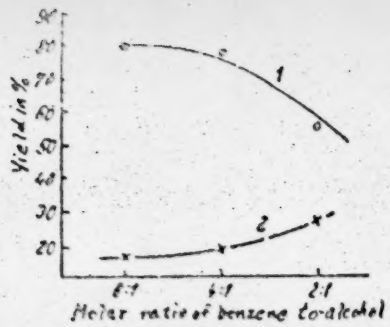

Fig. 3. Effect of molar ratio of benzene to isopropyl alcohol on the yield of the isopropylbenzene fraction with b.p. 145-160°. 1 - yield calculated on the isopropyl alcohol introduced; 2 - yield calculated on the benzene introduced.

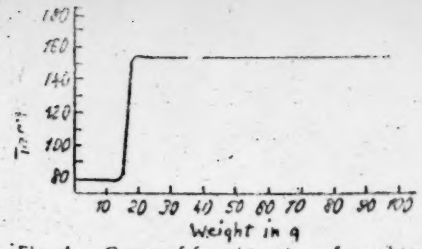

Fig. 4. Curve of fractionation of combined fractions with b.p. 85-145° and 145-160°.

Fractionation of the combined alkylbenzene fractions with b.p. 85-145° and 145-160° in a column with an efficiency of 25 theoretical plates gave 78% pure isopropylbenzene with b.p. 152-153°; n_D^{20} 1.4921 and d_4^{20} 0.8585 (Fig. 4). On the basis of the pure hydrocarbon the maximum yield of isopropylbenzene (b.p. 152-153°) is 66.3% of the isopropyl alcohol introduced.

TABLE 6

Influence of temperature on yield of isopropylbenzene fraction in the catalytic alkylation of benzene with isopropyl alcohol (Pressure 40 atm., molar ratio of benzene to alcohol = 4 : 1)

Expt. No.	Temperature (°C)	Weight of catalyzate (in g)	Results of fractionation of catalyzate (amount of fraction in g)					
			up to 85°	85-145°	145-160°			Residue (in g)
					in g	Yield in %		
						on benzene	on alcohol	
4	150	38.0	33.1	0.4	3.0	5.0	20.0	0.6
1	200	39.0	30.5	0.3	7.5	12.5	50.0	0.3
2	250	41.0	27.5	0.5	11.0	18.3	73.3	0.4
3	300	40.3	22.5	0.8	11.7	19.5	78.0	0.5
5	350	43.0	29.5	0.8	11.5	19.0	76.6	0.6

SUMMARY

1. Conditions were established for alkylation of benzene with diethyl ether, ethyl and isopropyl alcohols in contact with alumina-supported zinc chloride in the vapor phase at elevated pressure.

2. In the conditions established for the alkylation of benzene with diethyl ether the yield of broad-cut ethylbenzene fraction with b.p. 120-140° is 13-14% of the theoretical reckoned on the benzene taken and 74-86% on the reacted benzene.

3. Alkylation of benzene with ethylene gave ethylbenzene (b.p. 134-136°) in a yield of 14.7% of the theoretical reckoned on the benzene introduced into the reaction. Other reaction products were toluene and a mixture of diethylbenzenes consisting of 15.4% meta-isomer, 46.2% meta-isomer, and 38.1% para-isomer.

4. Alkylation of benzene with isopropyl alcohol in the selected conditions gave a 66.3% yield of isopropylbenzene (b.p. 152-153°) calculated on the alcohol taken.

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TRANSFORMATIONS OF VINYL ARYL ETHERS

COMMUNICATION 1. IONIC POLYMERIZATION OF VINYL ARYL ETHERS

A. V. Bogdanova and M. F. Shostakovsky

Vinyl aryl ethers with the formula $CH_2 = CH - OAr$ – have been little studied. Development of methods for their preparation and utilization involves a study of the processes of activation of the molecules of these substances. It is known that the activation of chemical compounds may proceed under the influence of substances capable of decomposing into ions or free radicals. On this basis the ability of an organic compound to react under the influence of ionic catalysts or radical initiators determines its reactivity to a considerable extent.

Investigation of various transformations and properties of vinyl aryl ethers permits clarification of the reactivity of these compounds and comparison of the reactivity with that of vinyl alkyl ethers. We commenced such an investigation with reference to the hydrolysis and hydrohalogenation of vinyl phenyl ether [1,2], to the addition of alcohols, and to the breakdown of its α-halo derivatives [3]. A study of these reactions showed that the reactivity of vinyl aryl ethers in presence of ionic catalysts is lower than that of vinyl alkyl ethers. For the purpose of fuller investigation of the transformations of vinyl aryl ethers we thought it expedient to study their polymerization and copolymerization both by ionic and radical mechanisms. These investigations throw adequate light on the chemical activation of molecules of vinyl aryl ethers and pave the way to synthesis of new derivatives of this series.

The experiments have shown that the reactivity of vinyl aryl ethers in polymerization processes under the influence of ionic catalysts is even more seriously inhibited than in the above-mentioned transformations.

The present communication is devoted to the ionic polymerization of vinyl aryl ethers, which is being studied by us in close connection with other transformations of vinyl ethers. Whereas the ionic polymerization of vinyl alkyl ethers has been adequately dealt with in the literature [4,5], the question of the polymerization of vinyl aryl ethers has up to now remained unclarified. Apart from a patent [6] and the exploratory study of Losev and co-workers [7], no investigations in this field have been reported.

As we have shown [1,2], hydrolysis and hydrohalogenation of vinyl phenyl ether in presence of ionic catalysts proceed with considerably greater difficulty than the corresponding reactions of vinyl alkyl ethers. This is because the activity of the ethereal oxygen is considerably weakened by the presence of the benzene ring, so that the formation (1), isomerization (2) and dissociation (3) of the oxonium complex proceed at a lower velocity:

$$CH_2 = CH - OAr + HX \longrightarrow CH_2 = CH - \underset{\displaystyle HX}{\overset{\displaystyle OAr}{|}} \qquad (1)$$

$$CH_2 = CH - \underset{\displaystyle HX}{\overset{\displaystyle OAr}{|}} \rightleftharpoons CH_2 - CHX - OAr \qquad (2)$$

$$CH_2 - CHX - OAr \longrightarrow CH_2 - \overset{+}{C}H - OAr + \overline{X}. \qquad (3)$$

The complex cation (3) formed during isomerization may give rise to transformations by a cationic mechanism. Reactions of addition, polymerization and copolymerization proceeding according to this mechanism can be represented by schemes (4) and (5):

$$CH_2 - \overset{+}{C}H - OAr + ROH \longrightarrow CH_2 - CH\begin{matrix} \diagup OAr \\ \diagdown OAr \end{matrix} + \overset{+}{H} \qquad (4)$$

$$CH_2 - \overset{+}{C}H - OAr + CH_2 = CH - OR \longrightarrow CH_2 - \underset{\displaystyle OAr}{\overset{\displaystyle }{CH}} - CH_2 - \underset{\displaystyle OR}{\overset{\displaystyle }{\overset{+}{C}H}} \qquad (5)$$

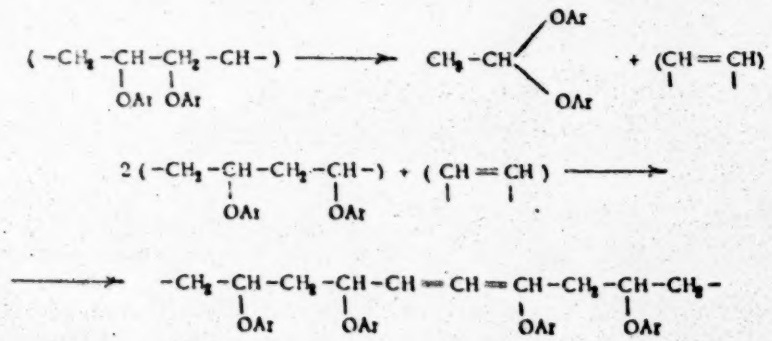
where R = Alk, Ar.

Compounds selected for study of copolymerization of vinyl aryl ethers were vinyl phenyl ether $CH_2=CH-OC_6H_5$ and vinyl p-tert-butylphenyl ether $CH_2=CH-OC_6H_4(C_4H_9\text{-tert})$. The catalysts used were protonic agents (FeCl$_3$, AlCl$_3$, and BF_3 etherate) either in the pure form or in the form of solutions of various concentrations and in various solvents. By varying the catalyst, the temperature, and the polymerization procedure, polymers of various molecular weights were obtained, ranging from oils to solids. Experiments were carried out in the range between 15° and the boiling point of the ether. Since the complex formed dissociates at different temperatures with different catalysts, the polymerization temperature is an important factor in this process. The most active catalyst in all cases was BF_3, probably due to the complex of vinyl ether with BF_3 having the lowest dissociation temperature.

Application of the method of purification of polymers of vinyl alkyl ethers to polyvinyl aryl ethers did not give satisfactory results. A method is proposed for purification and fractionation with the objective of obtaining pure products.

Vinyl aryl ethers differ from vinyl alkyl ethers in giving polymers which contain complex mixtures of homologous polymers. The presence of low-molecular fractions suggests the possibility of polymerization of, for example, vinyl phenyl ether taking place not by a chain mechanism but by a stepwise mechanism. In fact, the polymers of vinyl phenyl ether which were isolated included solid high-molecular fractions corresponding to the hexamer and higher. In this connection it was observed that with falling temperature of the experiment the yield of high-molecular fraction increased, and conversely. Thus the lowest yield of high-molecular fraction was obtained in experiments at the boiling point of the ether at atmospheric pressure, whereas on boiling in vacuum the yield of high-molecular fraction increased threefold.

For the purpose of a more detailed examination of the low-molecular fraction of polyvinyl phenyl ether, the latter was fractionated in vacuum and also subjected to molecular distillation. The objective was to isolate the individual compounds present in the original polymer or products of their transformation and breakdown. Vacuum fractionation of the low-molecular fraction of polyvinyl phenyl ether showed that in these conditions the polymer is decomposed with formation of diphenyl acetal and a resinous residue having a higher molecular weight than the original polymer. The rise of molecular weight of the residue may be caused by condensation of molecules of polymer and addition to them of the acetylenic bridge resulting from formation of diphenyl acetal. This possibility is supported by the increased carbon content of the residue. The proposed mechanism may be represented by the following hypothetical scheme.



(6)

Formation of similar acetylenic residues has been repeatedly observed in our laboratory with various substances and is probably characteristic of many derivatives of vinyl ethers. It was observed in the decomposition of β-chloroethylaryl ethers (3) as well as after ionic transformations of the vinyl ether of β-phenylaminoethanol (8). The acetylenic residue $-C\equiv C-$ which is formed on breakdown of the original product is a bridge which can consolidate the remaining molecules of the original substance.

Molecular fractionation of the low-molecular portion of polyvinyl phenyl ether gave a fraction which, judging by the data obtained, was a dimer. It is interesting that in this case, just as in that of vacuum fractionation, a condensed residue was obtained, but since the conditions of molecular fractionation excluded breakdown according to scheme (4), the carbon content of the nondistillable residue corresponded to the pure vinyl phenyl ether.

Polymers of vinyl p-tert-butylphenyl ether are solid, transparent and nearly colorless products, soluble in most organic solvents except methanol and ethanol. They also dissolve in mixtures of these alcohols with benzene and dioxan. This last circumstance makes impossible the separation of these polymers into fractions by the method of precipitation with alcohols. All the isolated polymers and their fractions were characterized by determination of the molecular weight, viscosity, solubility and elemental composition. The data are set forth in Tables 1 and 2.

TABLE 1

Characteristics of polymers of vinyl aryl ethers and their fractions

Serial number	Experimental conditions	Catalyst and its amount	Polymer isolated				Fraction I				Fraction II	
			% yield	outward appearance	mol. wt.	viscosity in centipoises	% yield	mol. wt.	viscosity in centipoises	m.p. (°C)	mol. wt.	viscosity in centipoises
1	Without heating 24 hours	1.5% dry $FeCl_3$	73.0	clear, viscous	383.5	0.6774	15.5	740.0	—	73-74	354.0	—
2	ditto	1.5% dry $AlCl_3$	80.2	Dark, m.p. 40-42	405.3	0.6781	11.0	1000.0	0.6836	61-63	349.0	0.7004
3	ditto	0.1% $BF_3(C_2H_5)_2O$	68.0	Clear, viscous	373.5	0.7969	—	—	—	—	—	—
4	At the boil under atm. pressure 1 hr.	0.012% FeCl (solution in dioxan)	70.5	Dark, viscous	351.0	0.6787	6.3	680.0	—	—	333.0	0.6797
5	At the boil in vacuum 2.5 hours	0.12% $FeCl_3$ (solution in dioxan)	94.0	Clear viscous	349.0	0.6752	15.0	965.2	0.6936	86-88	286.0	0.6764
6	At the boil in vacuum 1 hour	0.02% $BF_3(C_2H_5)_2O$ (solution in dioxan)	86.0	Clear, viscous	355.0	0.6960	7.8	756.0	0.7042	76-78	317.0	—

TABLE 2

Solubility of polymers of vinyl aryl ethers and their fractions*

Solvent	Polymer of vinyl phenyl ether	Fr. I of polymer of vinylphenyl ether	Fr. II of polymer of vinylphenyl ether	Polymer of vinyl-p-tert-butylphenyl ether
Acetone	+	X	+	+
Benzene	+	+	+	+
Toluene	+	+	+	+
Dioxan	+	+	+	+
Ether	+	X	+	+
Butyl alcohol	–	–	–	+
Ethyl alcohol	–	–	–	–
Methyl alcohol	–	–	–	–
Ethyl acetate	+	+	+	+
Vinyl phenyl ether	+	+	+	+
Vinyl butyl ether	+	+	+	+
Acetic acid	X	–	+	+
Gasoline (straight run)	–	–	X	+
Sunflower, olive oil	+	–	+	+
Ethylene glycol monoethyl ether	X	–	+	+

* + soluble X not completely soluble; – insoluble

EXPERIMENTAL *

The starting vinyl aryl ethers had the following constants: vinyl phenyl ether: b.p. 155-156°; n_D^{20} 1.5225; d_4^{20} 0.9772. vinyl p tert-butylphenyl ether: b.p. 219-220°; n_D^{22} 1.5102; d_4^{20} 0.9332.

Polymerization of vinyl phenyl ether

Without heating in the presence of $FeCl_3$, $AlCl_3$ or BF_3 etherate. An ampoule containing 10 g vinyl phenyl ether and 0.15 g dry catalyst or 1 ml 8% solution of $FeCl_3$ in dioxan or 0.5 ml 10% solution of BF_3 etherate in diethyl ether was left at 15-18°. Marked rise of viscosity was observed after 30 min. for BF_3 and after 3 hours for $FeCl_3$. When the viscosity had ceased to change, the polymer was extracted with a solvent or decanted and subjected to purification, dehydration and fractionation (details below). Yields and characteristics of the polymers and their fractions, obtained by this method, are set forth in Table 1.

With boiling under atmospheric pressure with $FeCl_3$ as catalyst. 30 g vinyl phenyl ether was placed in a three-necked flask fitted with stirrer, thermometer, dropping funnel and reflux condenser. At 155-156° (boiling point) dropwise addition was made in the course of 30 min. of 0.1 ml 4% solution of $FeCl_3$ in dioxan; during this operation the temperature in the flask gradually rose to 187°, after which it began to fall. In one-half hour after the catalyst had been added, stirring was stopped and the viscous, dark polymer was removed and subjected to purification and fractionation.

Found %: C 79.82; 79.70, H 6.90; 6.82
Calculated %: C 79.97 H 6.72 C_8H_8O.

* Senior Assistant M. S. Egorova assisted in the experimental work.

Yield of polymer 70.5%. Characteristics of the polymer and fractions are given in Table 1.

With boiling of the ether in vacuum, in presence of $FeCl_3$. Polymerization in vacuum was effected in a three-necked flask fitted with a reflux condenser and a Vigreux column, a thermometer, a capillary reaching to the bottom, and a trap placed between the condenser and the pump and cooled to −20°. The flask was heated on a petroleum jelly bath.

To 30 g vinyl phenyl ether at 56° (22 mm) (b.p. of the ether) was added dropwise in the course of 10 min. 0.9 ml of 4% solution of $FeCl_3$ in dioxan. After 2.5 hours' heating of the ether to 62-72° (20 mm), the colored but transparent polymer was worked up in the usual way to give 26.4 g very viscous, clear polymer.

Found %: C 80.40; 80.53; H 6.76; 6.91
Calculated %: C 79.97; H 6.72 C_8H_8O.

Yield of polymer 94.0%. Characteristics of the polymer and of its fractions are given in Table 1.

With boiling of the ether in vacuum, in presence of BF_3 etherate. To 50 g vinyl phenyl ether at 59° (17 mm) was added 3 drops of 15% solution of BF_3 etherate in dioxan. After 40 min. the temperature started to rise gradually to 92° (16 mm) in the course of 30 min. At the end of this period, a stream of ammonia gas was passed through the polymer to neutralize the catalyst, and the very viscous, colorless, transparent polymer was worked up in the usual way to give 43 g polymer (86.0% of the theoretical).

Found %: C 79.93; 79.87; H 6.66; 6.59
Calculated %: C 79.97; H 6.72 C_8H_8O.

Purification of the polymers of vinyl aryl ethers

The crude polymer discharged from the reaction flask was treated (in the usual steam distillation apparatus) with steam. In this way 400-500 ml (for 50 g polymer) aqueous distillate was taken off, which contained unpolymerized vinyl aryl ether, traces of phenol and acetaldehyde. After separation from the aqueous layer, the polymer was a clear, viscous product which was dehydrated by dissolving in benzene to form a 30% solution. The solution was filtered through a paper filter and the benzene was distilled off from the transparent solution at 40-50 mm. The residue was dried in a vacuum-desiccator at 10 mm and 50° to constant weight. The polymer obtained in this manner was a transparent, clear product.

Fractionation and examination of fractions of polyvinyl phenyl ether

Fractionation of polyvinyl phenyl ether prepared with BF_3 in vacuum. 10.25 g dry polyvinyl phenyl ether was dissolved in 40 g benzene (dioxan could also be used). To each 60 ml methanol placed in a 200 ml conical flask was added 5 ml of the polymer solution; on shaking quickly, a white, clotty precipitate came down which was separated by filtration through a glass filter. After washing with methanol and drying in a vacuum-desiccator to constant weight, the separated fraction (I) was a white, light powder (0.8 g). The solvent was driven off from the filtrate and the residue dried in vacuum to form a clear, transparent, viscous polymer (9.5 g) (fraction II). The characteristics are given in Table 1.

Examination of the low-molecular fraction II. a) Fractionation at 14 mm. 12.0 g fraction II was fractionated in vacuum to give a fraction with b.p. 98-130° (14 mm), weight 2.3 g, residue 8.8 g.

From the obtained fraction was separated 0.4 g (3.3%) crystalline phenol and 1.7 g (14.2%) diphenyl acetal with the constants: b.p. 150-151° (16 mm), n_D^{20} 1.5585; d_4^{20} 1.0870.

The undistillable residue was a brittle, amber-colored resin with m.p. 45-47°, odorless, soluble in diethyl ether, vinyl phenyl ether, dioxan and benzene; insoluble in gasoline and alcohols.

Found M: 473.0; 457.0
Calculated M: 506.59 $(C_8H_8O)_4\,C_2H_2$.
Found %: C 81.23, 81.36; H 6.99, 7.11
Calculated %: C 80.70; H 6.80 $(C_8H_8O)_4\,C_2H_2$.

b) Fractionation in high vacuum. 57 g of fraction II of polyvinyl phenyl ether was fractionated in a molecular still. The following fractions were collected:

Fraction I, b.p. to 100° ($5-10^{-3}$ mm); 11.2 g
Fraction II, b.p. 100-140° ($5-10^{-3}$ mm); 18.0 g.
Fraction III, b.p. 140-168° ($3-10^{-3}$ mm); 2.0 g ; Residue 19.0 g.

For fraction I was found M: 224.0, 227.4. Fraction II was a faintly colored, viscous product, free from odor, soluble in the majority of organic solvents except ethanol.

Found M: 233.0; 240.0
Calculated M: 240.28 $(C_8H_8O)_2$.
Found %: C 79.47; 79.70, H 6.75; 6.99
Calculated %: C 79.97; H 6.72 C_8H_8O.

For fraction III was found M: 266.8; 268.3. The residue was a brittle solid with m.p. 45-50°, soluble in ether, acetone, benzene, dioxan, vinyl ethers, [illegible]tly soluble in acetic acid and insoluble in gasoline and alcohols.

Found %: C 79.91, 79.96; H 6.94; 6.89
Calculated %: C 79.97; H 6.72 C_8H_8O.
Found M: 470.6; 484.4.
Calculated M: 481.12 $(C_8H_8O)_4$.

Polymerization of vinyl p-tert-butylphenyl ether

Without heating, in presence of dry $FeCl_3$. 5 g vinyl p-tert-butylphenyl ether and 0.05 g (1%) $FeCl_3$ were left at room temperature for 24 hours. 4.6 g (92% of the theoretical) solid, clear product was isolated with m. p. 42-44°.

Found %: C 81.21; 81.37, H 8.80; 8.99
Calculated %: C 81.77; H 9.15 $C_{12}H_{16}O$.
Found M: 471.20
Calculated M: 528.75 $(C_{12}H_{16}O)_2$

Without heating, in presence of BF_3 etherate. 5.2 g vinyl p-tert-butylphenyl ether and 3 drops of 16% solution of BF_3 etherate in dioxan [0.2% $BF_3(C_2H_5)_2O$] was left for 24 hours. 4.3 g (80% of the theoretical) clear, solid polymer was isolated, this possessed properties similar to the polymer isolated in the previous experiment.

With boiling in vacuum in presence of BF_3 etherate. To 30 g vinyl p-tert-butylphenyl ether at the boil (94° and 8 mm) in the course of 30 min. was added 6 drops of 16% solution of BF_3 etherate in dioxan [0.06% $BF_3(C_2H_5)_2O$]. During the next hour the temperature in the flask rose to 124° at 8 mm (at a bath temperature of 175°) and then began to fall. The ether changed into a clear, green-colored viscous mass which solidified on cooling. 26.0 g (86.7%) of clear, solid polymer with m.p. 40-41° was obtained after purification and drying.

Found %: C 81.62; 81.62; H 9.18; 9.23.
Calculated %: C 81.77; H 9.15 $C_{12}H_{16}O$.
Found M: 452.1; 457.5
Calculated M: 528.75 $(C_{12}H_{16}O)_3$.

The viscosity of this polymer was 0.7082 centipoise. The solubility of the polymer of vinyl p-tert-butylphenyl ether is given in Table 2.

SUMMARY

1. The catalytic action of $FeCl_3$, $AlCl_3$ and $BF_3(C_2H_5)_2O$ on vinyl aryl ethers was studied. It was established that catalytic action on the vinyl aryl ether is developed at temperatures between 15° and the boiling point of the ether.

2. Conditions were established for preparation of polymers of vinyl phenyl and vinyl p-tert-butylphenyl ethers which permitted quantitative yields of polymers.

3. Methods are proposed for purification and separation of polyvinyl phenyl ethers which enable isolation of products of various degrees of polymerization. The characteristics of the isolated polymers and their fractions are given.

4. A study was made of the behavior of the low-molecular fractions of polymers of vinyl phenyl ether in the conditions of vacuum distillation. A probable mechanism of their breakdown in these conditions is advanced.

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T.p. = C.B. translation pagination.

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TRANSFORMATIONS OF VINYL ARYL ETHERS

COMMUNICATION 2. RADICAL POLYMERIZATION AND COPOLYMERIZATION OF VINYL ARYL ETHERS

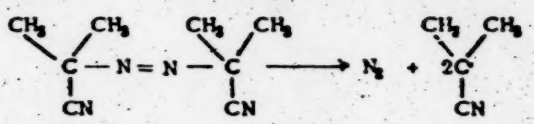
M. F. Shostakovsky and A. V. Bogdanova

The investigation of the conditions of polymerization of vinyl aryl ethers by a radical mechanism is a continuation of the study of the reactivity of compounds of this series. For this purpose we also studied the copolymerization of vinyl aryl ethers with vinyl alkyl ethers. Joint polymerization of these compounds is a valuable synthetic method of preparation of high-molecular substances with diverse properties on the one hand, and offers the possibility of comparing the reactivity of the original monomers on the other hand.

In the preceding communication [1] we described the polymerization of vinyl aryl ethers under the influence of ionic catalysts and compared the behavior of these compounds with that of vinyl alkyl ethers. Both the polymerization reactions and other ionic transformations of vinyl aryl ethers [2,3] show that the activation of their molecules is in Inhibition of activation of vinyl aryl ethers under the influence of ionic catalysts stage is an analogy with substances which are activated with the help of radical initiators. This prompted us to attempt to activate the molecules of vinyl aryl ethers with an agent which easily breaks down into free radicals. In the literature on the polymerization of vinyl ethers [4] the possibility of such a polymerization is denied in principle, and consequently vinyl ethers have been classed among the compounds which polymerize solely in presence of ionic catalysts.

It is known [5,6] that vinyl alkyl ethers can be made to copolymerize with substances which polymerize under the action of peroxide initiators. Such a phenomenon was also observed in the case of α-methylstyrene [7]. But none of these data relate to vinyl aryl ethers.

In the present communication we submit the results of an investigation of reactions of polymerization and copolymerization of vinyl phenyl and vinyl p-tert-butylphenyl ethers with vinyl ethyl and vinyl butyl ethers. The initiator selected for starting free radical reactions was azoisobutyronitrile, which breaks down into free radicals according to the scheme:



(1)

The radicals formed are also activators of the start of various processes and, in particular, of polymerization and copolymerization according to the scheme:

(2)

where Ar = C_6H_5; C_6H_4 (C_4H_9 tert.).

The fact that polymers and copolymers are formed supports the above-mentioned suggestion that vinyl aryl ethers can be activated by radical initiators. This fact, together with the previously noted inhibition of ionic reactions of vinyl aryl ethers, justifies the conclusion that in their degree of reactivity these compounds (II) occupy a position intermediate, as it were, between vinyl esters (I) and vinyl alkyl ethers (III):

$CH_2=CH-OCOAlk$ (I) $\qquad$ $CH_2=CH-OAr$ (II) $\qquad$ $CH_2=CH-OAlk$ (III)

Polymers of vinyl aryl ethers obtained in presence of azoisobutyronitrile (Table 1) are solid, transparent, faint-yellow products, soluble in the majority of organic solvents except alcohols. Purification, drying and fractionation of the polymers were effected by the procedure previously described for polyvinyl aryl ethers prepared

by ionic polymerization [1]. The composition and properties of the isolated products were determined by elementary analysis, molecular weight determinations, and examination of solubility in various solvents (Table 2). Table 2 includes for comparison the solubilities of polymers of vinyl ethyl and vinyl butyl ethers found by Gladyshevsky.

TABLE 1

Polymerization of vinyl phenyl ether in presence of azoisobutyronitrile

Amount of catalyst, in %	Experimental temperature, in °C	Duration, in hours	Yield of polymer, in %	Found				Formula	Calculated			
				mol. wt.	C %	H %	N %		mol. wt.	C %	H %	N %
1.0	80	280	7.2	787.0	78.07	7.18	—	$C_8H_8O_5C_8H_{12}N_2$	736.9	78.23	7.11	—
4.0	60	100	14.0	805.0	78.80	6.93	2.5	$C_8H_8O_6C_4H_6N$	788.9	79.16	6.90	1.78
4.0	75	100	21.6	894.0	79.06	7.15	1.8	$C_8H_8O_7C_4H_6N$	909.0	79.27	6.88	1.53
Fr. 1 from expr. 1		—	17.1	1833.0	79.18	6.87	1.5	$C_8H_8O_{14}C_8H_{12}N_2$	1818.2	79.27	6.87	1.53

Copolymers of vinyl aryl ethers differ from their polymers in being soluble in alcohols and gasoline, in being viscous products and in having, as a rule, a higher molecular weight; the latter is characteristic of all polyvinyl alkyl ethers. The polymer of vinyl para-tert-butylphenyl ether is soluble in ethyl alcohol and partly soluble in methyl alcohol. The composition of the isolated copolymers shows that copolymerization of vinyl aryl and vinyl alkyl ethers in presence of azoisobutyronitrile is accompanied by formation of polymeric products containing a considerably higher percentage of vinyl aryl ethers than of vinyl alkyl ethers, notwithstanding that in all cases the amount of vinyl aryl ether taken was less than or equal to that of the vinyl alkyl ether. This circumstance enables comparison of the reactivity of vinyl ethers.

In the course of investigation of the isolated polymers, it was established that more high-molecular fractions can be separated from polyvinyl phenyl ether. A fraction as isolated, for example, which corresponded to a tetradecamer, while the low-molecular fraction corresponded to a pentamer. The presence in the prepared polymers of various polymer - homologs supports the hypothesis [1] of the stepwise reactions of vinyl aryl ethers.

As was shown by the experiments on polymerization of vinyl phenyl ether in presence of azoisobutyronitrile the amount of the latter and the temperature and duration profoundly affect the yield of polymer (see Table 1). Intensification of all these factors caused only a small rise in molecular weight of the polymers. In all experiments on polymerization and copolymerization the unreacted portions of the original monomers were recovered unchanged.

EXPERIMENTAL*

The constants of the starting vinyl ethers are set forth in Table 3.

Polymerization of vinyl aryl ethers in presence of azoisobutyronitrile.

1. Polymerization of vinyl phenyl ether. 15 g of vinyl phenyl ether and 0.6 g (4 %) azoisobutyronitrile were sealed into an ampoule which was heated in a thermostat to 75° for 100 hours. The contents of 14 such ampoules, which were heated simultaneously (210 g vinyl phenyl ether), were fractionated with steam. 170 g vinyl phenyl ether (b.p. 155-156°, n_D^{20} 1.5230) was recovered. In the residue was a light-yellow solid which was freed from catalyst by twice treating with boiling methyl alcohol; it was then dried to constant weight in a vacuum-desiccator. Yield 45.4 g (21.6% of the theoretical) of polymer of vinyl phenyl ether with m.p. 48-49° (in capillary). Viscosity of polymer 0.5971 centipoise.

Found %: C 79.06, 79.09; H 7.15, 7.12; N 1.57; 2.0
Calculated %: C 79.27; H 6.88 N 1.53 $(C_8H_8O)_7C_6H_6N$.
Found M: 903.7; 885.0
Calculated M: 909.0 $(C_8H_8O)_7C_6H_6N$.

Fractionation of polymer. Separation into fractions of the prepared polymer was performed by the previously described procedure [1]. From 9.7 g polymer of vinyl phenyl ether was isolated:

*Senior technician M.S. Egorova took part in the experimental work.

TABLE 2

Solubility of polymers and copolymers of vinyl aryl ethers prepared in presence of azoisobutyronitrile •

Solvent	Polymer of vinyl phenyl ether	Copolymer of vinyl phenyl ether with vinyl ethyl ether	Polymer of vinyl ethyl ether.	Copolymer of vinyl phenyl ether with vinyl butyl ether	Polymer of vinyl butyl ether	Copolymer of vinyl p-tert-butyl-phenyl ether with vinyl butyl ether	Polymer of vinyl p-tert-butyl phenyl ether.
Acetone	+	+	+	+	+	+	+
Benzene	+	+	+	+	+	+	+
Toluene	+	+	+	+	+	+	+
Dioxane	+	+	+	+	+	+	+
Diethyl ether	+	+	+	+	+	+	+
Butyl alcohol	–	X	+	+	+	+	+
Ethyl alcohol	–	X	+	–	+	+	X
Methyl alcohol	–	–	–	–	–	X	X
Ethyl acetate	+	+	+	+	+	+	+
Vinyl phenyl ether	+	+	+	+	+	+	+
Vinyl butyl ether	+	+	+	+	+	+	+
Acetic acid	+	+	+	+	+	+	+
Straight-run gasoline	–	–	+	+	+	+	+
Ethylene glycol monoethyl ether	+	X	–	+	–	+	+

• + soluble; X partly soluble; – insoluble

TABLE 3

Ether	b.p. in deg C.	n_D^{20}	d_4^{20}
Vinyl phenyl	155-156	1.5225	0.9770
Vinyl p-tert-butylphenyl	219-220	1.5102	0.9332
Vinyl butyl	93-93.5	1.4020	0.7790
Vinyl ethyl	36-36.5	1.3780	0.7530

For Fraction II , m.p. 44-45°

Found %: N 2.13 2.19;
Calculated %: N 2.10 $(C_8H_8O)_8C_4H_8N$.

Fr. I., 1.9 g (17.1 % of theoretical).
Fr. II., 7.3 g (75.2% of theoretical).

Both fractions were solid, transparent, brittle products.

For Fraction I, m.p. 69-70°

Found %: C 79.27; 79.09
H 6.86; 6.88: N 1.4; 1.6
$(C_8H_8O)_{14}C_8H_{12}N_2$.
Calculated %: C 79.27;
H 6.87; N 1.53
Found M: 1766.0; 1900.0;
$(C_8H_8O)_{14}C_8H_{12}N_2$. Calculated M: 1818.2

Found M: 653.6, 647.9
Calculated M: 666.9 ($C_8H_8O)_5C_4H_6N$.

2. Polymerization of vinyl p-tert-butylphenyl ether. From 75 g vinyl p-tert-butylphenyl ether and 3.0 g (4%) azoisobutyronitrile, in the conditions of the above-described experiment, were isolated 58.5 g unreacted monomer with b.p. 109-110° (15 mm), n_D^{20} 1.5090 and 13.5 g (17.6% yield) polymer with m.p. 48-49°. Viscosity of polymer 0.7036 centipoises.

Found %: C 79.69, 79.91, H 8.83; 9.13; N 1.82; 1.97
Calculated %: C 80.48; H 9.42; N 2.34 ($C_{17}H_{16}O)_5C_4H_6N$.
Found M: 572.3, 580.2
Calculated M: 596.83 ($C_{17}H_{16}O)_5C_4H_6N$.

Copolymerization of vinyl aryl ethers with vinyl alkyl ethers

1. Copolymerization of vinyl phenyl ether with vinyl butyl ether. A mixture of 10 g (0.08 mole) vinyl phenyl ether, 10 g (0.1 mole) vinyl butyl ether and 0.4 g (2%) azoisobutyronitrile was sealed into an ampoule and heated to 65-70° for 100 hours. From 10 such ampoules (200 g starting ethers) was recovered 170.0 g of mixture of monomers and 10 g (9.7%) of a light-yellow, transparent, very viscous polymer was isolated.

Found %: C 77.11, 77.25; H 8.35, 8.28, N 1.38; 1.52
Found M: 743.0; 735.2

The viscosity of the polymer was 0.7190 centipoise. The copolymer contains: 60.5 (mole-%) vinyl phenyl ether and 39.5% vinyl butyl ether.

2. Copolymerization of vinyl phenyl ether with vinyl ethyl ether. In the conditions of the preceding experiment 100.0 g (0.83 mole) vinyl phenyl ether, 72.0 g (1.0 mole) vinyl ethyl ether and 3.4 g (2%) azoisobutyronitrile were heated in ampoules to give 142.0 g monomers and 16.1 g (9.3% of the theoretical) of a clear, nearly solid polymeric product.

Found %: C 77.48, 77.40; H 7.92; 7.76; N 1.54; 1.74
Found M: 718.7; 724.1

Viscosity of copolymer 0.7038 centipoise. The copolymer contains: 71.65 mole-% vinyl phenyl ether and 28.35 mole-% vinyl ethyl ether.

3. Copolymerization of vinyl p-tert-butylphenyl ether with vinyl butyl ether. A mixture of 16.4 g (0.1 mole) vinyl p-tert-butylphenyl ether, 10 g (0.1 mole) vinyl butyl ether and 1.05 g (4%) azoisobutyronitrile was sealed into an ampoule and heated to 70-75° for 100 hours. From 5 such ampoules (122 g starting ethers) was recovered 100.8 g of a mixture of monomers while 18.33 g (11.6% of the theoretical) of light-yellow, very viscous product was isolated.

Found %: C 77.98; 78.10; H 9.88; 9.88, N 1.78; 1.79
Found M: 539.5, 530.8

The viscosity of the copolymer was 0.7108 centipoise. The copolymer contains 73.0 mole-% vinyl p-tert-butylphenyl ether and 27.0 mole-% vinyl butyl ether.

SUMMARY

1. The possibility is demonstrated of polymerization and copolymerization of vinyl aryl ethers under the influence of a radical initiator—azoisobutyronitrile.

2. It is shown that in presence of this initiator vinyl aryl ethers can be made to copolymerize with vinyl alkyl ethers.

3. Polymers of vinyl phenyl and vinyl p-tert-butylphenyl ethers, also their copolymers with vinyl ethyl and vinyl butyl ethers, were isolated and characterized. A probable mechanism of their formation is advanced.

4. It is found that vinyl aryl ethers exhibit greater reactivity in copolymerization reactions than vinyl alkyl ethers.

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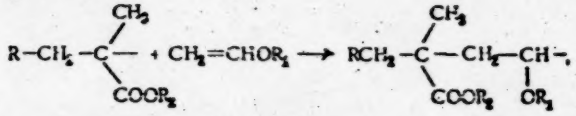
CHEMICAL TRANSFORMATIONS OF UNSATURATED AND HIGH-MOLECULAR COMPOUNDS

COMMUNICATION 3. COPOLYMERIZATION OF METHACRYLIC ACID AND ITS METHYL ESTER WITH VINYL PHENYL ETHER

M. F. Shostakovsky and A. M. Khomutov

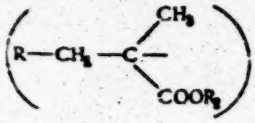
In our previous communications we described the copolymerization of methacrylic acid and its methyl ester with vinyl alkyl ethers [1, 2, 3]. These investigations established that vinyl alkyl ethers enter into copolymerization with methacrylic acid and its derivatives under the influence of benzoyl peroxide notwithstanding that they themselves are not susceptible to polymerization under the influence of oxygen and peroxides. On these observations was based the hypothesis that the initiator of the formation of copolymers of unsaturated components is not a product of breakdown of benzoyl peroxide (C_6H_5, C_6H_5COO; $-O-$), but a complex radical formed on interaction of $C_6H_5COO^{\bullet}$ with methacrylic acid or its esters.

This radical also promotes the polymerization and copolymerization of the original monomers and, in particular, of vinyl alkyl ethers. As we know [4], vinyl ethers do not become activated under the influence of oxygen, peroxides and hydroperoxides in polymerization processes. Notwithstanding that this fact has been adduced in the literature [5] to deny the possibility of free-radical transformations of vinyl ethers, we hold directly opposed views. We think that it is necessary to take account of the nature and specificity of the atoms, of the semi-dissociated molecules and of the free radicals which initiate the process; also of the fact that atomic and molecular oxygen ($-O-$, $-O-O-$), as well as products of breakdown of peroxides and hydroperoxides of the type of C_6H_5COO- do not cause activation of vinyl ethers since their valence belongs to the oxygen. The possibility of formation of $C_6H_5COO^{\bullet}$ by symmetrical cleavage of benzoyl peroxide has been indicated in the literature [6]. Consequently, the nature of the radical and its free valence is the same in these cases and belongs to the oxygen: $-O-$, $-O-O-$; C_6H_5COO-. Evidently, these radicals have little activity for involving vinyl ethers in polymerization and copolymerization reactions. Moreover, transformations of vinyl ethers can take place under the influence of free radicals when the free valence of the latter belongs to carbon, in which case the formation of a polymer chain may be represented by the following schemes:



where R is a radical obtained from benzoyl peroxide; R_1 – is the corresponding alkyl or aryl; R_2 – is a methyl group or hydrogen.

The great activity of this radical



is accounted for by its chemical structure and, among other reasons, by the presence of conjugated double bonds $-C=C$ and $C=O$ [7]. The activity of methyl methacrylate as a copolymerization component has been illustrated in many examples [8].

Great interest is attached to the study of the above-mentioned properties with reference to new representatives of vinyl ethers, for example vinyl phenyl ether: $CH_2=CHOC_6H_5$. In contrast to the vinyl alkyl ethers, vinyl phenyl ether polymerizes with difficulty by an ionic mechanism, due to the influence of the benzene ring and the structure of the molecule which causes the oxygen to lose its electron-donating properties and hinders the catalytic action of, for instance, hydrogen chloride [9]. Furthermore, we must mention that vinyl phenyl ether is susceptible

to thermal polymerization [10]. All these points of difference between vinyl phenyl ether and vinyl alkyl ethers justify a special study of the former in copolymerization reactions with methacrylic acid and its methyl ester.

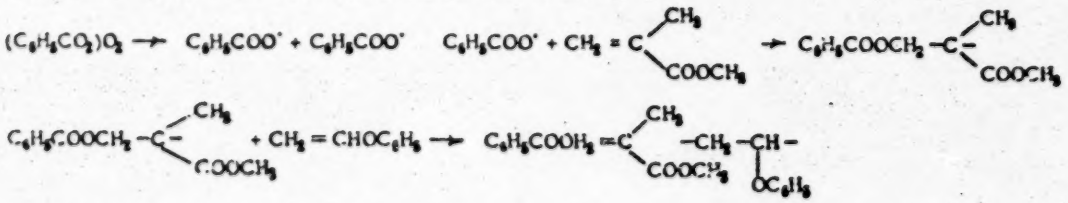
A study of the conditions of polymerization of methyl methacrylate and vinyl phenyl ether in various molar ratios showed that with increasing concentration of vinyl phenyl ether the reaction in some cases proceeds differently than with vinyl alkyl ethers. In all cases substances were obtained which corresponded in elementary composition to products of copolymerization of the original components. Change in the concentration of vinyl phenyl ether led to an increase of the number of vinyl phenyl ether links in the chain of the molecule (see table). It was furthermore established that with molar ratios of 3 : 1 and 1 : 1 of methyl methacrylate to vinyl phenyl ether, copolymers were obtained whose degree of polymerization did not exceed that of polymethyl methacrylate. At a 1:3 ratio, i.e., with an excess of vinyl phenyl ether, the polymerization reaction is hindered and low-molecular polymers are formed.

Content of original monomers in mole-%		Yield in %	C in %	H in %	Molar composition of links of molecules		Viscosity	
$CH_2=C(CH_3)COOCH_3$	$CH_2=CHOC_6H_5$				$-CH_2-C(CH_3)(COOCH_3)-$	$-CH_2-CH(OC_6H_5)-$	η_{abs} st/sec	$\eta_{rel.}$
100	–	97.5	60.03 60.05	8.30 8.28	100	–	0.011	1.5011
75	25	76.0	62.70 62.70	7.95 8.16	88.49	11.51	0.021	2.8932
50	50	51.7*	64.42 64.34	7.85 7.98	81.05	19.95	0.015	2.0432
25	75	10.56	67.85 67.10	7.65 7.39	65.38	34.62	0.0081	1.0930
–	100	–	–	–		None		

* 8.21 g vinyl phenyl ether was separated and the amount of methyl methacrylate was found to be 1.07 g.

The evaluation of the degree of polymerization or copolymerization of the investigated products was based on comparison of the viscosity of the solutions of the polymers and copolymers in question. This comparison shows that the viscosities of the solutions of the investigated copolymers is higher than the viscosity of solutions of the corresponding polymers of methyl methacrylate obtained in the same conditions (see table). Copolymers obtained with excess of vinyl phenyl ether, however, have a low viscosity (table). Clearly in this case there is a slowing-down of the formation of chains (table), the yields of copolymers being reduced with increasing concentration of vinyl phenyl ether in the reaction medium. At the same time there is a qualitative change in the copolymer chain due to rise in the number of links of vinyl phenyl ether. Examination of the products of copolymerization shows that separated polymerization is not observed in these conditions and that, in particular, no polymer of methyl methacrylate is formed in these experiments. The resultant copolymers differ from polymers of methyl methacrylate in respect of solubility, for example in a 1 : 1 mixture of butanol and vinyl phenyl ether, and in fusibility.

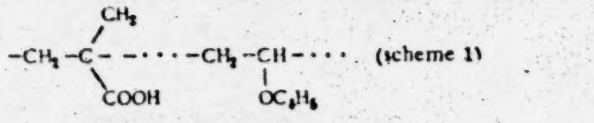
Consequently, the present investigation has shown that vinyl ethers react according to a free-radical mechanism with a radical whose free valences are attached to carbon:

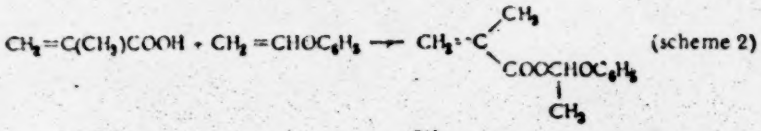


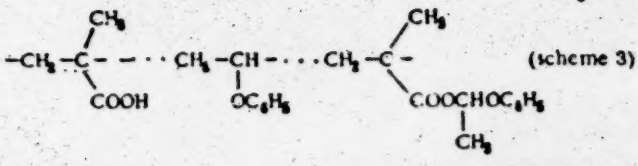
i.e., the nature has been clarified of the radicals which can or cannot involve vinyl ethers in a copolymerization reaction.

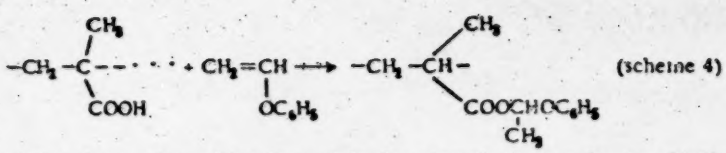
We now go on to consider the data on reaction of methacrylic acid with vinyl phenyl ether. The investigations shows that several concurrent reactions take place in the conditions described below. The reaction mixture contains, apart from copolymers, the original monomers, acylals and phenoxyethylidene methacrylate. The copolymer molecules contains links of: methacrylic acid, vinyl phenyl ether and acylal.

Consequently the copolymerization reaction (scheme 1) is accompanied by formation of acylals (scheme 2); in addition, vinyl alkyl ethers can add on to the carboxyl of polymethacrylic acid (scheme 4):


(scheme 1)


(scheme 2)


(scheme 3)


(scheme 4)

The isolated copolymers have a low molecular weight; for example the copolymers obtained from molar ratios of monomers have a molecular weight of 2265. The yields of copolymers were low.

On the basis of the above observations it follows that reaction of methacrylic acid with vinyl phenyl ether is accompanied by the same types of reactions as in the case of reaction of methacrylic acid with vinyl alkyl ethers [1].

EXPERIMENTAL

The starting materials for the investigations were freshly distilled: methyl methacrylate with b.p. 99.5 - 100°, n_D^{20} 1.4150; d_4^{20} 0.936, methacrylic acid with b.p. 160°; n_D^{20} 1.4313; d_4^{20} 1.0159; acid value 550 mg KOH; vinyl phenyl ether, b.p. 155°, n_D^{20} 1.5225; d_4^{15} 0.9765. Benzoyl peroxide was purified by two reprecipitations; acetone with b.p. 56.5°; n_D^{20} 1.3595 methanol with b.p. 64-65°; n_D^{20} 1.3300; benzene with b.p. 80 - 80.5°; n_D^{20} 1.5010.

Experimental Procedure

Copolymerization was carried out in glass ampoules which were heated in a thermostat at a temperature of 60 ± 1°. The starting substances were brought into reaction in various molar ratios in presence of 0.2% benzoyl peroxide reckoned on the total weight of monomers. The process proceeded continuously until solid or highly viscous products had been formed. At the conclusion of the reaction the ampoules were cooled at 0°. In the same conditions control experiments were run with benzoyl peroxide and, separately, methacrylic acid, methyl methacrylate, and vinyl phenyl ether. The solid reaction products were purified by numerous dissolutions and precipitations until a negative reaction was obtained for the double bond. The polymers and copolymers were then dried to constant weight. The copolymers were not subjected to selective reprecipitation since a polymer of methyl methacrylate was not found. The copolymers were analyzed for C and H. On the basis of the data obtained, calculations were made of the composition of the copolymers. In addition, the fusibility and viscosity were determined [11]. Solutions obtained after precipitation of the copolymers were analyzed for their content of methyl methacrylate, fractional distillation was applied for separation of the vinyl phenyl ether; part of the solution was evaporated (under vacuum) to establish the possible presence of polymers soluble in a mixture of precipitant and solvent.

Below are presented some data of investigations of the polymerization and copolymerization of various molar ratios of methyl methacrylate to vinyl phenyl ether. In addition, methyl methacrylate and vinyl phenyl ether were separately treated in the same conditions as their mixtures. Methyl methacrylate polymerized. Vinyl

phenyl ether did not polymerize and the original ether was collected after fractionation.

Copolymerization of $CH_2=C(CH_3)COOCH_3$ and $CH_2=CHOC_6H_5$ (1:1 molar ratio). 11.4 g methyl methacrylate and 13.6 g vinyl phenyl ether were taken for copolymerization. The mixture of starting monomers was heated for 40 hours. The reaction products had a viscous consistency. The conditions of copolymerization and the method of purification are set forth above. The copolymer is soluble in a mixture of butanol and vinyl phenyl ether (1:1); the pure polymer of methyl methacrylate does not dissolve in this mixture. The copolymer was completely freed from monomers (test with bromine water), and then dried to constant weight at 30 - 35° (4 mm). The copolymers were analyzed for C and H. The copolymer does not break down when heated, but melts. Yields, composition and viscosities of the copolymers are set forth in the table.

The solution obtained after precipitation of the copolymer was analyzed for its content of methyl methacrylate (by hydrolysis), and the residue from the analysis was fractionally distilled. The fractionation gave a substance with b.p. of 184.5° n_D^{20} – 1.5220 d_4^{20} 0.9672, which agree with the constants of vinyl phenyl ether.

Methyl methacrylate was also copolymerized with vinyl phenyl ether in the above-described conditions but with a molar ratio of 3:1. The properties of the resultant polymer resembled those of the polymer described above. Yield and composition of the copolymer are set forth in the table.

Copolymerization of $CH_2=C(CH_3)COOCH_3$ and $CH_2=CHOC_6H_5$ (molar ratio of 1:3) was performed in the above-described conditions. After heating for 40 hours the reaction product was a faintly colored liquid. A preliminary attempt to precipitate the polymer from this liquid by addition of methanol and water was unsuccessful; the liquid was therefore fractionally distilled at 75-80° (35 mm) in presence of hydroquinone. In this way 0.95 g substance was collected in a cooled trap, and 12.5 g in the receiving flask; in the distillation flask remained 10.85 g viscous liquid. The substance in the trap had n_D^{20} 1.4165, similar to that of methyl methacrylate; the fraction in the receiver had n_D^{20} 1.5220, corresponding to vinyl phenyl ether. The viscous liquid in the distillation flask was dissolved in acetone; on adding methanol a precipitate came down which was purified from polymers, dried to constant weight and subjected to elementary analysis.

The molecular weight was determined by the cryoscopic method: M = 1563.4 1662.5. The values of molecular weight and the relative viscosity enabled calculation of the magnitude of the constant K_m, which was found to be $0.62 \cdot 10^{-4}$.

We now go on to describe the experimental results of copolymerization of methacrylic acid with vinyl phenyl ether.

Copolymerization of $CH_2=C(CH_3)COOH$ and $CH_2=CHOC_6H_5$ (molar ratio of 3:1). Amounts of reactants taken were 17.2 g methacrylic acid and 7.9 g vinyl phenyl ether in presence of 0.05 g benzoyl peroxide. The reaction conditions were those described above. After heating for 60 hours, the contents of the ampoule had not changed in outward appearance, i.e., they were still liquid. Samples of the liquid were mixed with methanol, benzene, gasoline and diethyl ether but formation of a precipitate or development of turbidity were not observed. The liquid was distilled in vacuum in presence of hydroquinone. At 75-80° (35 mm) 17 g liquid came over which consisted of 12.5 g methacrylic acid and 4.5 g vinyl phenyl ether. In the distillation flask remained a viscous liquid (7.8 g). The latter was dissolved in a mixture of 95% acetone and 5% methanol. Precipitation of the polymer was effected with gasoline (70-80° boiling range). The polymer was then worked up according to the usual procedure. Yield of copolymer 2.5 g. Its elementary analysis gave: %C 66.19; 66.00, H 7.33; 7.32; which corresponds to a molecule containing 57.88% methacrylic acid links and 42.12% vinyl phenyl ether links. The percentage content in the molecules was 62.2 and 37.8 respectively. The copolymer was analyzed for carboxyl groups by the titration method. The methacrylic acid content of the copolymer was found to be 57.19%, in good agreement with the value calculated from the elementary analysis. The acetaldehyde in the copolymer was determined and the value converted to vinyl phenyl ether; the amount of the latter so found was 5.13%.

The solution obtained after precipitation of the copolymer was evaporated in vacuum; evaporation of the solvent left 1.35 g liquid which after fractional distillation had n_D^{20} 1.5028; it was phenoxyethylidene methacrylate [12].

Copolymerization of $CH_2=C(CH_3)COOH$ and $CH_2=CHOC_6H_5$ (molar ratio of 1:1). 10.38 g methacrylic acid, 14.50 g vinyl phenyl ether and 0.05 g benzoyl peroxide were mixed together. The reaction conditions were as described above. The reaction mixture contained a polymer (test by precipitation with gasoline) which was precipitated with gasoline and washed with methanol. The polymer was dried to constant weight. Its

elementary analysis gave (in %): C 69.49, 69.40; H 6.94, 6.93, which corresponds to a copolymer containing 42 wt.-% methacrylic acid and 58 wt.-% vinyl phenyl ether. The copolymer was analyzed for its acetaldehyde content but none was detected. It follows that acylal groupings are absent from the chain of the molecule. The molecular weight of the copolymer as determined by the cryoscopic method was 2265.

Copolymerization of $CH_2=C(CH_3)COOH$ and $CH_2=CHOC_6H_5$ (molar ratio of 1:3). 4.75 g methacrylic acid, 20.25 g vinyl phenyl ether and 0.05 g benzoyl peroxide were heated together for 60 hours. At the conclusion of the heating the mass was distilled in presence of hydroquinone (test for polymer with methanol and gasoline did not give a precipitate). 12.15 g vinyl phenyl ether was collected at 75° (30 mm). The residue in the distillation flask was dissolved in acetone and precipitated with gasoline (distilled at 70-80°). A polymer was separated and weighed 3.5 g after purification and drying. The copolymer had the elementary composition (in %): C 67.04, 67.07; H 6.81, 6.83.

On the basis of the elementary analysis calculations were made of the composition of the copolymer: the content of methacrylic acid links in the molecule is 53.5%, that of vinyl phenyl ether links 46.5%. The content of methacrylic acid links determined by the titration method was 52.03%. Determination of the acetaldehyde and its recalculation to vinyl phenyl ether gave a content of the latter of 10.26%.

The solution obtained after precipitation and purification of the copolymer was evaporated and distilled: from the solution was isolated 2.76 g phenoxyethylidene methacrylate with n_D^{20} 1.5034.

SUMMARY

1. Copolymers of methacrylic acid and methyl methacrylate with vinyl phenyl ether have been prepared.

2. The composition of the copolymers was found to depend upon the concentration of vinyl phenyl ether in the reaction mixture.

3. It was shown that the copolymerization reaction is accompanied by side reactions with formation of acylals.

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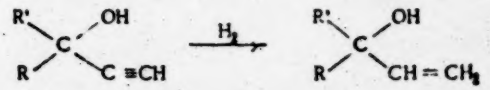
DERIVATIVES OF TERTIARY UNSATURATED ALCOHOLS

COMMUNICATION 2. SYNTHESIS OF METHYL-, ETHYL-, ISOPROPYL -, AND BUTYLDIMETHYLVINYLACETALS

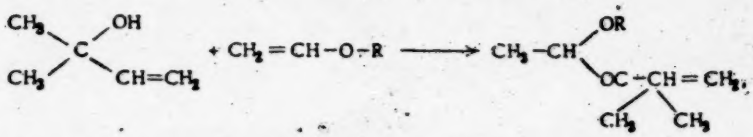
M. F. Shostakovsky and I. A. Nikhiev

A. E. Favorsky and his school [1] have established the conditions for synthesis of substituted allyl alcohols according to the scheme:



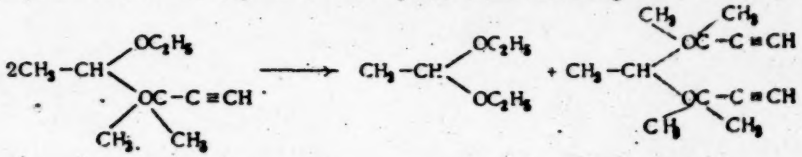
These compounds are valuable starting materials in synthetic organic chemistry [2].

The authors of the present paper aimed at synthesizing substituted allyl acetals on the basis of substituted allyl alcohols and vinyl alkyl ethers according to the scheme:

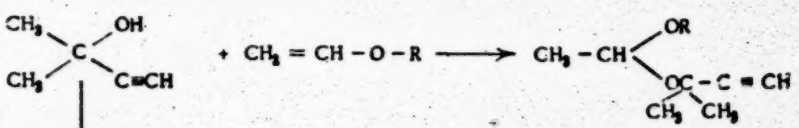


where R = CH_3; C_2H_5; C_3H_7 (iso) and C_4H_9.
Acetals of this series are of great interest and have scarcely been studied.

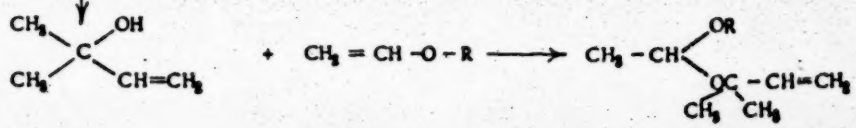
In our previous communication [3] it was shown that reaction of dimethylethynylcarbinol with vinyl ethyl ether leads to disproportionation of the unsymmetrical acetylenic acetal according to the following scheme:



In the present investigation we compare the properties of the acetylenic and the corresponding substituted allyl acetals. The synthesis of these (V) and other (VI) acetals is based on reaction of dimethylethynylcarbinol and of dimethylvinylcarbinol with vinyl alkyl ethers according to the scheme:



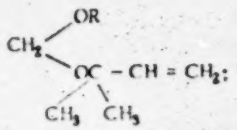
(V)



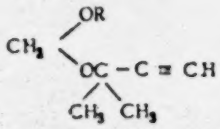
(VI)

These acetals were prepared in presence of a catalyst in the conditions described in the previous communication [3]. This interesting transition from acetylenic acetals to the corresponding substituted allyl acetals and the investigation of their properties enables us to study the reactivity and stability of these compounds.

One of us [4] has carried out similar investigations of acetylenic and the corresponding substituted allyl formals, when it was established that the substituted allyl formals (VII) are more stable than the acetylenic formals (VIII):



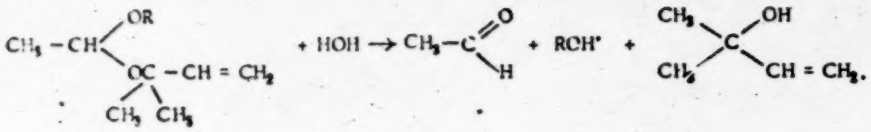
(VII)



(VIII)

Finally, it was of interest to verify and amplify the general concepts about the properties of acetylenic substituted allyl acetals and the corresponding formals.

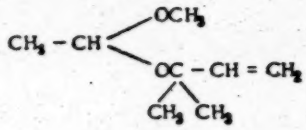
To sum up, therefore, the present investigation has shown that substituted allyl acetals are more stable than the corresponding acetylenic acetals. The structure of the prepared acetals was confirmed by their cleavage to the original components according to the scheme:



EXPERIMENTAL*

The following starting materials were used in the synthesis: dimethylvinylcarbinol with b.p. 98-99°; n_D^{25} 1.4140; d_4^{20} 0.8246; vinyl methyl ether with b.p. 5.5°; n_D^{6} 1.3730; d_4^{0} 0.7725; vinyl ethyl ether with b.p. 36°; n_D^{20} 1.3779; d_4^{20} 0.7531; vinyl isopropyl ether with b.p. 55°; n_D^{20} 1.3862; d_4^{20} 0.7520; vinyl butyl ether with b.p. 93-94°; n_D^{25} 1.4026; d_4^{20} 0.7792.

1. Synthesis of methyldimethylvinylacetal (I)



In an ampoule cooled to −12 to −14° were placed 21.5 g (0.25 mole) dimethylvinylcarbinol, 16 g (0.277 mole) vinyl methyl ether and a sealed capillary containing 0.016 mg 30% hydrochloric acid. After sealing the ampoule, the capillary was broken by shaking. The ampoule was then heated in a thermostat at 65° for 9.5 hours. The next day the ampoule was cooled to −10° and opened; the contents were neutralized with calcined potassium carbonate and distilled. The volatile fraction was collected in a trap cooled to −10 to −14°; the following were collected

Fr. I., b.p. to 27° (9-10 mm); 3.2 g; n_D^{20} 1.4122

Fr. II., b.p. 28-29° (9-10 mm), 132-133° (760 mm); 28g; n_D^{20} 1.4130 (yield 78%)

The material in the trap was 2.7 g vinyl methyl ether with traces of dimethylvinylcarbinol.

Examination of fraction II. Fraction II had d_4^{20} 0.8601; n_D^{20} 1.4130; Found MR 41.75; Calculated for $C_8H_{16}O_2$ MR 41.963. Found M 138.8; 132.5; Calculated M 144.

Found %: C 66.73; 66.98; H 11.09; 11.18

Calculated %: C 66.66; H 11.11 $C_8H_{16}O_2$.

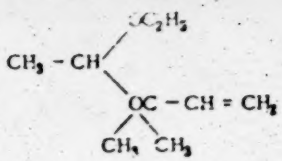
The data correspond to those for methyldimethylvinylacetal (I) which is a colorless liquid with an ethereal odor. The acetaldehyde content of the acetal was determined by the bisulfite method.

Found: acetaldehyde 94.02 and 93.8% of the theoretical.

Vinyl methyl ether was synthesized by P. V. Tyupaev to whom we convey our thanks.

* Senior Assistant Z. S. Volkova participated in the work.

2. Synthesis of ethyldimethylvinylacetal (II)



To a mixture of 43 g (0.5 mole) dimethylvinylcarbinol and 36 g (0.5 mole) vinyl ethyl ether at room temperature and with constant stirring was added 0.012 ml 30% hydrochloric acid (during this operation the temperature rose to 52°), after which the mixture was left overnight. The next day the reaction mixture was dried with potassium carbonate and the filtered product (79.0 g) was distilled. The volatile products were collected in a trap cooled to −15 to −16°.

Fr. I., b.p. 21-26° (11-12 mm); 2.2 g; n_D^{20} 1.4152.
Fr. II., b.p. 40-41° (11-12 mm); 146-147° (760 mm); 65 g ; n_D^{20} 1.4119 (yield 82.82%)
Residue − 1.4 g.

The material in the trap was mainly unreacted vinyl ethyl ether (8.0 g) with traces of dimethylvinylcarbinol.

Examination of fraction II. The fraction with b.p. 40-41° had: d_4^{20} 0.8502; n_D^{20} 1.4119; Found MR 46.22; Calculated for $C_9H_{18}O_2F$ MR 46.581; Found M 149.0 ; 147.3; Calculated M 158.

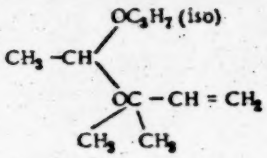
Found %: C 68.22, 68.30, H 11.97, 11.89.
Calculated %: C 68.35 , H 11.39 $C_9H_{18}O_2$.

The acetaldehyde content of the acetal was also determined by the bisulfite method.

Found : acetaldehyde 97.98 and 97.43% of the theoretical.

The above data correspond to ethyldimethylvinylacetal (II).

3. Synthesis of isopropyldimethylvinylacetal (III)



Exactly the same ratios of starting substances were used for this synthesis as for the preceding synthesis (II). After addition of 0.012 ml hydrochloric acid the temperature of the mixture rose to 62°. After working up and distillation by the above-described method, 68 g product was obtained with b.p. 45-46° (10-11 mm) and 156-157° (760 mm) with the following constants: d_4^{20} 0.8422; n_D^{20} 1.4126; Found MR 50.88; calculated for $C_{10}H_{20}O_2F$ MR 51.199; Found M 163.50; 164.7 ; Calculated M 172.0.

Found %: C 69.96 69.76; H 11.30; 11.48.
Calculated %: C 69.76; H 11.62. $C_{10}H_{20}O_2$.
Found acetaldehyde 95.26 and 97.98% of the theoretical.

The above data correspond to isopropyldimethylvinylacetal (III); yield 79.06% of theory.

4. Synthesis of butyldimethylvinylacetal (IV)

With constant stirring 0.012 ml hydrochloric acid was added to a mixture of 21.5 g (0.25 mole) dimethylvinylcarbinol and 25 g (0.25 mole) vinyl butyl ether. The temperature rose to 70°. Working up and distillation by the above procedure gave 38.5 g product (yield 80.8%) with b.p. 182-183°; d_4^{20} 0.8396; n_D^{20} 1.4148; Found MR 55.46; Calculated for $C_{11}H_{22}O_2F$ MR 55.817; Found M 180.0; 179.1; Calculated M 186.

Found %: C 70.98; 71.00; H 11.01 10.97.
Calculated %: C 70.96; H 11.18 $C_{11}H_{22}O_2$.
Found acetaldehyde 99.80 and 96.93% of the theoretical.

The constants found correspond to butyldimethylvinylacetal . It should be mentioned that all of the four substituted allyl acetals are stable, possess a characteristic ethereal odor and decolorize a weak solution of $KMnO_4$ and bromine water. The properties of the prepared acetals are being studied.

SUMMARY

1. For the first time the methyl-, ethyl-, isopropyl- and butyldimethylvinylacetals have been prepared and characterized.

2. It was established that the substituted allyl acetals are more stable than the acetylenic acetals.

3. The structure of the substituted allyl acetals was confirmed by their hydrolytic cleavage into the original components.

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[3] M. F. Shostakovsky and I. A. Shikhiev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, No. 6, 1061.**

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* See C.B. translation, page 61.

** " " " " 843.

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DESTRUCTIVE HYDROGENATION OF TOLUENE UNDER HIGH HYDROGEN PRESSURE

M. G. Gonikberg and V. E. Nikitenkov

In 1929 Hoffman and Lang [1] published a short communication on their experiments on destructive hydrogenation of toluene in the absence of catalysts in an autoclave at 470-485° and a hydrogen pressure of up to 200-250 atm. Under these conditions up to 50% of the toluene is converted into benzene; the gaseous reaction product contained, apart from hydrogen, methane and ethane. Also present among the reaction products (in very small amounts) were diphenyl, monomethyldiphenyl and ditolyl. Hydrogenation of toluene to methylcyclohexane was not observed. In experiments carried out in the absence of hydrogen at 470°, the authors observed the formation in small quantity of hydrogen and ditolyl.

In 1938 Nemtsov [2] published the results of an investigation of the homogeneous destructive hydrogenation of toluene under hydrogen pressure at temperatures close to 500° (the pressure range was not indicated). According to Nemtsov's data the reaction velocity does not depend upon the presence of a metallic packing and to a first approximation may be expressed by an equation for bimolecular reaction between toluene and hydrogen. The constant K_2 of the bimolecular reaction satisfies the equation:

$$\log K_2 = 15.54 - \frac{66000}{4.57\,T},$$

where K_2 is expressed in liters·mole^{-1}·min^{-1}.

Calculation of the exponential factor by the theory of collisions led the author to the conclusion that each active collision brings about transformation of 60 molecules of hydrocarbon. Nemtsov did not consider, however, that a chain mechanism involving the intermediate formation of atoms or free radicals was likely to account for this fact.

In the present research the homogeneous destructive hydrogenation of toluene was studied at 455-490° and at hydrogen pressures up to 1350 atm. On the basis of the results obtained, a chain mechanism is advanced for this process.

EXPERIMENTAL

Apparatus and experimental procedure

The investigation was carried out in an autoclave of stainless steel with a capacity of about 160 ml and fitted with a hydraulic seal. The toluene was charged into the reactor which was then sealed; the pressure of the hydrogen was thereupon raised with the help of a pressure apparatus fed from a gasholder. The toluene was previously distilled in a rectifying column with an efficiency of 30 theoretical plates and was characterized by the following constants: b.p. 110.4–110.6° (760 mm); n_D^{20} 1.4963. According to the literature [3]: it has b.p. 110.626° (760 mm); n_D^{20} 1.49693.' The initial hydrogen pressures in the different experiments varied between 100 and 600 atm. The reactor was then placed in an electric furnace and heated to the required temperature which was measured with a thermocouple in a long sheath inside the reactor and passing through the hydraulic seal. The temperature was kept constant to ±2°. The reactor was held at the experimental temperature for a specified period and then cooled with water. The working pressure ranged from 280 to 1350 atm. At the conclusion of the experiment the pressure was slowly dropped to atmospheric; the liquid products were fractionated in a rectifying column with an efficiency of 30 theoretical plates. When the initial hydrogen pressures were 100 and 250 atm. (working pressure 280 and 650 atm.), the liquid reaction products contained benzene and toluene together with about 1% of high-boiling components; in the majority of experiments carried out with an initial hydrogen pressure of 450 and 600 atm. (working pressure 1100 and 1350 atm), methylcyclohexane was found in the reaction products in addition. Chromatographic separation of the aromatic hydrocarbons from the methylcyclohexane fraction followed by refractionation of the latter gave pure methylcyclohexane (b.p. 100.7-100.9° (760 mm); n_D^{20} 1.4229; d_4^{20} 0.7690; the literature [3] reports: b.p. 100.937° (760 mm); n_D^{20} 1.42305; d_4^{20} 0.76936.

Results of the investigation

a) Influence of duration of experiment and the pressure upon the reaction velocity. Results of experiments at 455° using a constant amount of toluene (30 g) charged into the reactor are set forth in Table 1. The yield of benzene at constant hydrogen pressure increases substantially linearly with the duration of the experiment (Fig. 1). In the last column of Table 1 are set forth the ratios of reaction velocity to hydrogen concentration (in hour^{-1}). Within the limits of error this ratio remains constant for each experimental series (at constant pressure), but de-

creases with rising pressure (concentration) of hydrogen. Thus the reaction velocity increases with rising hydrogen concentration, although not proportionally to the latter but slightly more slowly. For example, with a 3.8-fold increase of hydrogen concentration the reaction velocity rises approximately 2.5 times.

It follows from the data of Table 1 that homogeneous destructive hydrogenation of toluene is not a bimolecular reaction, for which the velocity would necessarily have been proportional to the concentration of toluene and hydrogen

TABLE 1

Destructive hydrogenation of toluene at 455 ° and various hydrogen pressures

P_{H_2} atm. (working)	Duration, in hours	Yield of benzene		Amount of hydrogen in moles			$\frac{\text{moles } C_6H_6}{\text{moles } H_2 \cdot \tau}$ (mean) hour^{-1}
		in mol-%	in mole	initial	final	mean	
280	3	10.7	0.0349	0.557	0.522	0.539	0.0215
280	5	12.6	0.0409	0.557	0.516	0.536	0.0153
290	7	23.3	0.0761	0.585	0.509	0.547	0.0199
290	8	26.0	0.0845	0.585	0.500	0.542	0.0195
280	11.6	34.9	0.114	0.557	0.443	0.500	0.0196
650	3••	19.8	0.0645	1.290	1.226	1.258	0.0171
"	5	32.6	0.106	1.290	1.184	1.237	0.0171
"	7	43.5	0.142	1.290	1.148	1.219	0.0166
"	10.5	65.1	0.212	1.290	1.078	1.184	0.0170
1100	3	23.2	0.0755	2.110	2.035	2.073	0.0122
"	3	24.1	0.0787	2.110	2.031	2.070	0.0127
"	3	19.2	0.0625	2.110	2.048	2.079	0.0101
"	5	38.5	0.126	2.110	1.984	2.047	0.0123
"	5.5	43.6	0.142	2.110	1.968	2.039	0.0126
1350	3.5	33.4	0.109	2.690	2.581	2.635	0.0118
"	3.5	32.5	0.106	2.690	2.584	2.637	0.0114
"	5.5	58.4	0.191	2.690	2.409	2.595	0.0134

• Calculated on the yield of benzene.

•• Mean of 4 experiments.

b) Influence of initial toluene concentration upon the reaction velocity. The dependence of the reaction velocity on the toluene concentration was examined by carrying out experiments at 455° with various initial charges of toluene (20,30 and 40 g). The hydrogen concentration during this series did not vary by more than 10 % from the mean value. Results of these experiments are set forth in Table 2.

It follows from Table 2 that the reaction velocity increases with increasing toluene concentration; the values in the last column, however, indicate the absence of direct proportionality between the concentration of (charged in) toluene and the reaction velocity. A twofold increase of the charge of toluene in one experimental series speeded up the reaction 1.58 times; in a second series the speed increased 1.44 times; the average speed-up was 1.5 times; consequently the reaction velocity is approximately proportional to the square root of the toluene concentration. This effect could not be deduced from inspection of the data of Table 1 due to the relatively small changes of mean concentrations of toluene during the majority of the experiments in each series.

TABLE 2

Destructive hydrogenation of toluene at 455° and various initial concentrations of toluene

P_{H_2} in atm. (working)	Duration in hours.	Charge of toluene, in g	Yield of benzene in mole-%	Yield of benzene in mole	Amount of hydrogen, in moles initial	Amount of hydrogen, in moles final	Amount of hydrogen, in moles mean	moles C_6H_6 / moles $H_2 \cdot \tau$ hour^{-1}
270	8,5	20	31,2	0,0678	0,612	0,544	0,578	0,0138
290	8	30	26,0	0,0845	0,585	0,500	0,542	0,0195
290	8,5	40	26,6	0,0851	0,500	0,415	0,458	0,0219
640	5	20	43,5	0,0945	1,420	1,336	1,373	0,0138
650	5	30	32,6	0,106	1,290	1,184	1,237	0,0171
650	5	40	25,2	0,110	1,162	1,052	1,108	0,0198

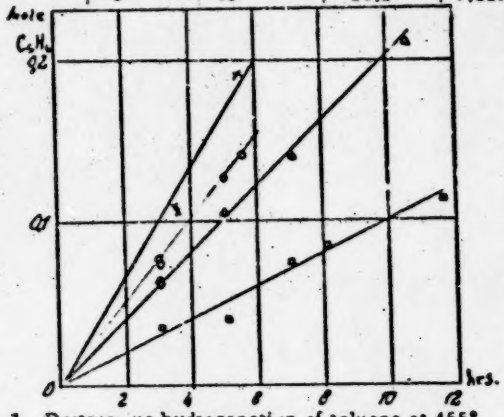

Fig. 1. Destructive hydrogenation of toluene at 455° under pressure: □ – 280 atm; Δ – 650 atm; ○ – 1100 atm; X – 1350 atm.

c. Investigation of the influence of the surface/volume ratio (S/V) on the reaction velocity. It was considered desirable to confirm the existing data for the homogeneity of the process under investigation. For this purpose experiments were carried out with addition of turnings from the same batch of stainless steel. The area of the surface of the turnings, evaluated from the measurement of the parameters of 100 cuttings, was about 18 cm^2/g. The area of the internal surface of the reactor was about 260 cm^2.

Below are set forth the results of an examination at 464° with an initial hydrogen pressure of 250 atm. and a reaction period of 4,25 hours:

S cm^2	260	400	900
S/V cm^{-1}	1.6	2.5	5.6
Yield C_6H_6, expressed as mol .-% to C_7H_8 charged	46.8	44.8	52.6

The conclusion to be drawn from these results is that the size of the surface and its ratio to the volume has no marked influence upon the reaction velocity. The slight increase in benzene yield at S/V = 5,6 is scarcely outside the limits of experimental error.

TABLE 3

Destructive hydrogenation of toluene at 490° (working pressure of 670 atm.)

τ duration in hours	Yield of benzene in mol. %	Yield of benzene in mole	Amount of hydrogen, in mole initial	Amount of hydrogen, in mole final	Amount of hydrogen, in mole mean	moles C_6H_6 / moles $H_2 \cdot \tau$ (mean) hour^{-1}
1	36,1	0,118	1,290	1,172	1,231	0,0958
1,5	50,1	0,163	1,290	1,127	1,209	0,0902
2	61,2	0,200	1,290	1,090	1,190	0,0840

d) Influence of temperature on the reaction velocity. Results of experiments carried out at 490° with a toluene charge of 30 g are set forth in Table 3.

Comparison of the data of Tables 1 and 3 shows that rise of temperature from 455 to 490° leads to a very considerable increase of reaction velocity. The energy of activation was not determined in this investigation.

e) Investigation of the high-boiling reaction products. It appeared of interest to investigate the high-boiling reaction products whose structure ought to give an indication of the radicals formed in the course of destructive

[illegible] examination of the high-boiling residues after rectification of the reaction products established the presence of diphenyl and ditolyl.

The isolated diphenyl was characterized by its m.p. of 68,5-70° (the literature gives 70,0°). A mixed test with pure diphenyl did not give a depression of m.p.

Results of analysis.
Found %: C 93.29; H 6.72
Calculated %: C 93.46; H 6.54 $C_{12}H_{10}$

Ditolyl was separated by fractionation of the high-boiling residue (fraction 277-280° at 760 mm); n_D^{25} 1,6003; d_4^{20} 1,0105.

Results of analysis.
Found %: C 92.35, 92.41; H 7.64, 7.52.
Calculated %: C 92.26, H 7.74. $C_{14}H_{14}$.

Oxidation of the ditolyl with chromic acid mixture gave terephthalic acid which was identified as the dimetnyl ester—m.p. of ester 138-139,5° (the literature gives 140°).

Results of analysis:
Found %: C 61.65; H 5.25
Calculated %: C 61.85; H 5.19. $C_{10}H_{10}O_4$.

Dibenzyl was not found among the reaction products. We carried out a special experiment to establish the causes of the absence of dibenzyl. 5 g dibenzyl was dissolved in 30 g benzene and subjected to high pressure (working pressure of 580-560 atm.) at 460° for 5 hours. Among the products of reaction was found only 1,34 g dibenzyl. In our experimental conditions, therefore, dibenzyl undergoes far-reaching destructive hydrogenation, and this may account for its absence from the products of reaction.

EVALUATION OF RESULTS

a) Thermal decomposition of toluene in absence of hydrogen.

In 1938 Szwarc [4] studied the induction period of thermal decomposition of toluene (from 0,01 to 1% decomposition) in vacuum at temperatures of 738-864° by passing toluene vapor through a heated quartz tube and cooling the reaction products. The gaseous reaction products comprised 59-62% hydrogen and 38-41% methane. The liquid reaction products contained benzene and dibenzyl (1 mole of dibenzyl to 1 mole of gas formed). The author arrived at the conclusion that the reaction involves the following steps:

$$C_6H_5CH_3 \xrightarrow{1} C_6H_5CH_2^{\cdot} + H^{\cdot}$$

$$C_6H_5CH_3 + H^{\cdot} \xrightarrow{2} C_6H_5CH_2^{\cdot} + H_2$$

$$C_6H_5CH_3 + H^{\cdot} \xrightarrow{3'} C_6H_6 + CH_3^{\cdot}$$

or

$$C_6H_5CH_3 + H^{\cdot} \xrightarrow{3''} C_6H_5^{\cdot} + CH_4$$

$$CH_3^{\cdot} + C_6H_5CH_3 \xrightarrow{4'} CH_4 + C_6H_5CH_2^{\cdot}$$

or

$$C_6H_5^{\cdot} + C_6H_5CH_3 \xrightarrow{4''} C_6H_6 + C_6H_5CH_2^{\cdot}$$

$$2C_6H_5CH_2^{\cdot} \xrightarrow{5} C_6H_5CH_2CH_2C_6H_5$$

The suggestion that rupture of the C – C bond

$$C_6H_5CH_3 \longrightarrow C_6H_5^{\cdot} + CH_3^{\cdot}$$

was the first step in the reaction was refuted by data for the composition of the gaseous reaction products (60% hydrogen), whereas the author's proposed scheme satisfactorily accounted for the formation of the above-mentioned compounds and for the amount of dibenzyl formed. Ditolyl was not detected.

As already indicated above, Hoffmann and Lang [1], who thermally decomposed toluene in an autoclave at 470° found ditolyl among the reaction products, but not dibenzyl. In the present research we, too, found ditolyl among

the products of thermal decomposition of toluene at 460°. The absence of dibenzyl may have been due to its thermal instability.

Of great interest is the formation of ditolyl during thermal decomposition of toluene. Detachment of hydrogen from the benzene ring by reaction under our experimental conditions

$$C_6H_5CH_3 \xrightarrow{1'} H^{\cdot} + C_6H_4CH_3^{\cdot}$$

is extremely improbable, although we cannot altogether exclude its possibility. It seemed to us, however, that formation of ditolyl may also be explained by supplementing Szwarc's scheme by the following reactions:

$$C_6H_5CH_3 + H^{\cdot} \xrightarrow{3'''} H_2 + C_6H_4CH_3^{\cdot}$$

$$C_6H_4CH_3^{\cdot} + C_6H_5CH_3 \xrightarrow{4'''} C_6H_5CH_3 + C_6H_5CH_2^{\cdot}$$

$$2C_6H_4CH_3^{\cdot} \xrightarrow{6} CH_3C_6H_4C_6H_4CH_3$$

The absence of ditolyl from the products of Szwarc's experiments may be accounted for by the very low velocity of reaction 3''' in vacuum. We carried out the decomposition of toluene at considerably lower temperatures than in Szwarc's experiments, but the duration of the experiments was 7 hours as against Szwarc's contact period of 0.3–0.9 sec, i.e., our reaction period was 100,000 times greater; the toluene pressure in our experiments was 325-370 atm, instead of 3 - 14 mm mercury, i.e., it was also tens of thousands of times higher than could occur for the velocity of reaction 3'''.

Reactions 3', 3'', and 3''', if they indeed take place, constitute an extremely interesting type of radical reactions. In recent years data have been obtained which makes reactions of this type highly probable. In an investigation of the mechanism of photolysis of biacetyl, Blacket and Bell [5] arrived at the following hypothesis for the reaction:

$$CH_3^{\cdot} + CH_3COCOCH_3 \longrightarrow CH_3COCH_3 + CH_3CO^{\cdot}$$

Gomer and Noyes [6] studied the photochemical breakdown of $Hg(CH_3)_2$ and concluded that the following reaction took place

$$CH_3^{\cdot} + Hg(CH_3)_2 \longrightarrow C_2H_6 + Hg + CH_3^{\cdot}$$

or

$$CH_3^{\cdot} + Hg(CH_3)_2 \longrightarrow A\,(\text{unstable complex})$$

$$CH_3^{\cdot} + A \longrightarrow C_2H_6 + Hg + 2CH_3^{\cdot}\ [\text{or } CH_3^{\cdot} + HgCH_3^{\cdot} \text{ or } Hg(CH_3)_2].$$

After analyzing the foregoing data, Darwent [7] suggested that reactions of the type in question involve addition of an atom or radical to the molecule with formation of an unstable free radical which then breaks down, for example

$$CH_3^{\cdot} + CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow CH_3-\overset{O^{\cdot}}{\overset{|}{\underset{CH_3}{C}}}-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow CH_3COCH_3 + CH_3CO^{\cdot}$$

If this hypothesis is accepted, then reactions 3', 3'', and 3''' could have occurred during the decomposition of toluene (depending evidently on the point of attack of the H atom).

Using the concepts discussed above, we are able to formulate a scheme for a chain mechanism of the destructive hydrogenation of toluene which is in satisfactory accord with the data which we obtained for the kinetics of this reaction.

b) Destructive hydrogenation of toluene. If we accept the proposed reaction scheme for thermal decomposition of toluene, then it is clear that in presence of hydrogen under pressure there will be interaction between radicals, formed by thermal decomposition, with molecular hydrogen (also with molecules of toluene and reaction products). Reaction with molecules of H_2 lead to formation of atomic hydrogen and in consequence to the development of a chain reaction.

We suggest the following scheme as probable for the destructive hydrogenation of toluene:

$$C_6H_5CH_3 \xrightarrow{1} C_6H_5CH_2^{\cdot} + H^{\cdot}\ \text{development of a chain}\ *$$

* We could also write: $C_6H_5CH_3 \xrightarrow{1'} C_6H_5CH_3^{\cdot} + H^{\cdot}$ (see above).

$$H^{\cdot} + C_6H_5CH_3 \xrightarrow{2} C_6H_5CH_2^{\cdot} + H_2$$

$$\xrightarrow{3} C_6H_4CH_3^{\cdot} + H_2$$

$$\xrightarrow{4} C_6H_6 + CH_3^{\cdot}$$

$$\xrightarrow{5} C_6H_5^{\cdot} + CH_4$$

$$H_2 + C_6H_5CH_2^{\cdot} \xrightarrow{6} C_6H_5CH_3 + H^{\cdot}$$

$$H_2 + C_6H_4CH_3^{\cdot} \xrightarrow{7} C_6H_5CH_3 + H^{\cdot}$$

$$H_2 + CH_3^{\cdot} \xrightarrow{8} CH_4 + H^{\cdot}$$

$$H_2 + C_6H_5^{\cdot} \xrightarrow{9} C_6H_6 + H^{\cdot}$$

$$C_6H_5CH_3 + C_6H_4CH_3^{\cdot} \xrightarrow{10} C_6H_5CH_2^{\cdot} + C_6H_5CH_3$$

$$C_6H_5CH_3 + CH_3^{\cdot} \xrightarrow{11} C_6H_5CH_2^{\cdot} + CH_4$$

$$C_6H_5CH_3 + C_6H_5^{\cdot} \xrightarrow{12} C_6H_5CH_2^{\cdot} + C_6H_6$$

$$H^{\cdot} + CH_4 \xrightarrow{13} CH_3^{\cdot} + H_2$$

$$H^{\cdot} + C_6H_6 \xrightarrow{14} C_6H_5^{\cdot} + H_2$$

$$2\,C_6H_5^{\cdot} \xrightarrow{15} (C_6H_5)_2$$

$$2C_6H_5CH_2^{\cdot} \xrightarrow{16} (C_6H_5CH_2)_2$$

$$2C_6H_4CH_3^{\cdot} \xrightarrow{17} (C_6H_4CH_3)_2$$

$$2CH_3^{\cdot} \xrightarrow{18} C_2H_6$$

Breaking of the chain

The reaction might also be called "cross" breaking with formation of ethylbenzene, xylene, methyldiphenyl, diphenylmethane and other products*. We have followed the course of reactions 15 and 17; Hoffmann and Lang [1] found ethane (reaction 18) among the reaction products as well as methyldiphenyl; concerning dibenzyl, we have shown (see above) that under our experimental conditions it suffers destructive hydrogenation.

We suggest that chain breaking during homogeneous destructive hydrogenation of toluene takes place preferentially at the tolyl radicals according to reaction 17.

Under steady conditions with considerable length of chain:

$$\frac{d(C_6H_4CH_3)}{d\tau} = K_3(H)(C_6H_5CH_3) - K_7(H_2)(C_6H_4CH_3) - K_{10}(C_6H_5CH_3)\cdot(C_6H_4CH_3) = 0.$$

Hence

$$(C_6H_4CH_3) = \frac{K_3(H)(C_6H_5CH_3)}{(H_2)\left[K_7 + K_{10}\frac{(C_6H_5CH_3)}{(H_2)}\right]} \qquad (1)$$

From the balance of chain initiation and breakage

$$K_1(C_6H_5CH_3) = K_{17}(C_6H_4CH_3)^2 \qquad (2)$$

* Here we do not write the reactions opposite to 11 and 12 (due to the low activity of benzyl radicals), nor the heterogeneous hydrogenation of toluene to methylcyclohexane.

we find, taking (1) into account:

$$(H) = \sqrt{\frac{K_1}{K_{17}}} \cdot \frac{K_7 + K_{10}\dfrac{(C_6H_5CH_3)}{(H_2)}}{K_3} \cdot \frac{(H_2)}{\sqrt{(C_6H_5CH_3)}} \quad (3)$$

We write the expression for the reaction velocity

$$w = (K_4 + K_5)(H)(C_6H_5CH_3) \quad (4)$$

or

$$w = \sqrt{\frac{K_1}{K_{17}}} \cdot \frac{(K_4 + K_5)}{K_3} \cdot (H_2) \cdot \sqrt{(C_6H_5CH_3)} \cdot \left[K_7 + K_{10}\frac{(C_6H_5CH_3)}{(H_2)}\right] \quad (5)$$

From this it appears that the reaction velocity to a first approximation (without allowing for the expression in the square brackets) must be proportional to the hydrogen concentration and to the square root of the toluene concentration. Taking into account the expression in the square brackets in equation (5), we reach the conclusion that the reaction velocity must increase slower than linearly with increasing hydrogen concentration. This has actually been observed to be the case.

It can be shown that equations analogous to (5) for the reaction velocity are also obtained on the assumption that preferential chain breaking occurs not at tolyl but at methyl and phenyl radicals, as well as with "cross" breakages with participation of these radicals. The reaction velocity equation takes on another form in the event of preferential chain breakage at benzyl radicals; we then have:

$$K_1(C_6H_5CH_3) = K_{16}(C_6H_5CH_2)^2 \quad (6)$$

$$(C_6H_5CH_2) = \frac{(C_6H_5CH_3)[K_8(H) + K_{16}(C_6H_5CH_2) + K_{11}(CH_3) + K_{12}(C_6H_5)]}{K_6(H_2)} \quad (7)$$

On the condition that reactions 13 and 14 can be neglected, we find:

$$CH_3 = \frac{K_4(H)}{K_{11} + K_8\dfrac{(H_2)}{(C_6H_5CH_3)}}; \qquad C_6H_5 = \frac{K_5(H)}{K_{12} + K_9\dfrac{(H_2)}{(C_6H_5CH_3)}}$$

$$(C_6H_5CH_2) = \frac{K_3(H)}{K_{10} + K_7\dfrac{(H_2)}{(C_6H_5CH_3)}}$$

Hence

$$w = \sqrt{\frac{K_1}{K_{16}}}(H_2) \cdot (C_6H_5CH_3) \times$$

$$\times \frac{K_6(K_4 + K_5)}{\left[K_6 + \dfrac{K_9K_{10}}{K_{10} + K_7\dfrac{(H_2)}{(C_6H_5CH_3)}} + \dfrac{K_8K_{11}}{K_{11} + K_8\dfrac{(H_2)}{(C_6H_5CH_3)}} + \dfrac{K_9K_{12}}{K_{12} + K_9\dfrac{(H_2)}{(C_6H_5CH_3)}}\right]} \quad (8)$$

Inspection of equation (8) leads to the conclusion that in the event of preferential chain breakage at the benzyl radicals, the reaction velocity must increase at a rate higher than is represented by a linear relation when the hydrogen concentration is increased. This is not confirmed by experiment. Consequently the kinetic considerations and the chemical investigation of the reaction products point to dibenzyl being formed under our experimental conditions only to an insignificant extent and without influencing the kinetics of the reaction.

Equation (5) and similar equations for preferential breakage at the methyl and phenyl radicals (derived on the assumption of the insignificant extents of reactions 13 and 14 which constitute the reverse of reactions 8 and 9)

are consistent with the experimental data obtained in the present investigation.

The authors express their thanks to A. E. Gavrilova for advice during the experimental work, and to V. V. Vevvedsky for advice and help in working out the scheme for the chain mechanism of the investigated reaction.

Assistance in the work was given by draftsman-designer A. A. Opekunov and fitter V. A. Kuznetsov.

SUMMARY

1. The homogeneous destructive hydrogenation of toluene was investigated at high hydrogen pressures.

2. A chain mechanism is advanced for the investigated process on the basis of which an equation for the reaction velocity is derived which is consistent with the experimental results.

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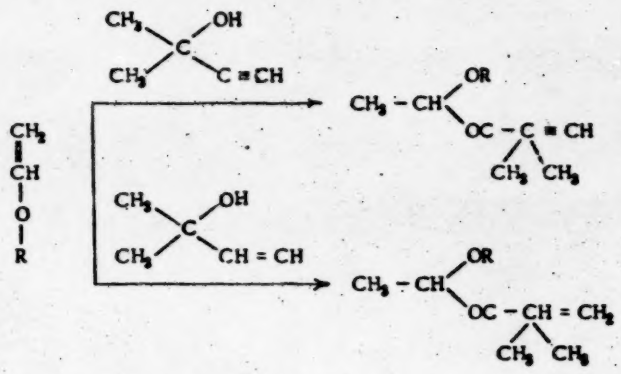
DERIVATIVES OF TERTIARY UNSATURATED ALCOHOLS

COMMUNICATION 3. SYNTHESIS OF DIMETHYLETHYNYL(VINYL)- AND METHYLETHYLETHYNYL(VINYL)-tert-BUTYL ACETALS

M. F. Shostakovsky, I. A. Shikhiev and V. I. Belyaev

The present investigation forms a continuation of our studies in the field of vinyl ethers [1]. With the objective of ascertaining the reactivity of vinyl ethers of tertiary alcohols, we have studied their reaction with tertiary acetylenic and olefinic carbinols.

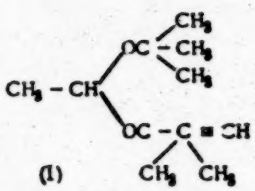
In our previous communications we established that vinyl ethers of primary and secondary alcohols in presence of traces of hydrochloric acid react with acetylenic [2] and olefinic [3] carbinols to form the corresponding acetals according to the scheme:



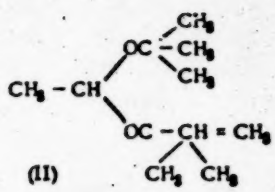
where R = CH_3; C_2H_5; C_3H_7 (iso) C_4H_9-(iso) and C_4H_9-n.

The constants of the prepared acetylenic and olefinic acetals exhibit the following regularities: 1) the boiling points of the olefinic acetals are lower than those of the corresponding acetylenic acetals; 2) the specific gravities and refractive indices of the olefinic acetals are also lower than those of the corresponding acetylenic acetals.

The aim of the present investigation was to synthesize and study the properties of the following acetylenic and olefinic acetals:



(I)



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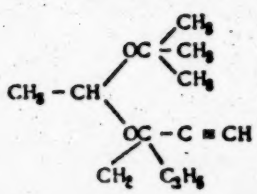
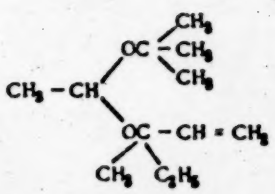


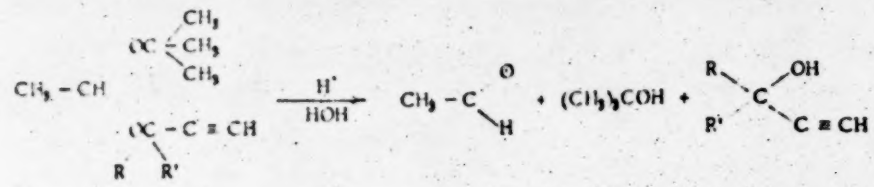
(III)



(IV)

The investigation resulted in the preparation and characterization of tert-butylmethylmethylethylethynyl acetal and tert-butylmethylmethylethylvinyl acetal. It was established that the prepared acetylenic and olefinic acetals, like those previously investigated [2,3], also exhibit regular differences in specific gravity and refractive index. It may be mentioned that the acetylenic acetals are less stable and turn yellow on standing, whereas the olefinic acetals remain clear after standing for the same period.

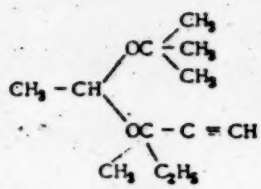
It has thus been shown that acetals containing the vinyl group are more stable. The structure of the prepared acetals was confirmed by their hydrolytic cleavage into the original components according to the equation:



EXPERIMENTAL*

The following starting substances were used for syntheses: vinyl-tert-butyl ether with b.p. 75-75.8°; n_D^{20} 1.3926; d_4^{20} 0.7699; dimethylethynyl carbinol [4] with b.p. 102-103°; n_D^{22} 1.4208; d_4^{20} 0.8580; dimethylvinyl carbinol [4] with b.p. 98-99°; n_D^{20} 1.4140; d_4^{20} 0.8242; methylethylethynyl carbinol [4] with b.p. 120-121°; n_D^{20} 1.4285; d_4^{20} 0.8697; methylethylvinyl carbinol [4] with b.p. 115-116°; n_D^{20} 1.4258; d_4^{20} 0.8375.

Synthesis of tert-butylmethylethylethynyl acetal



To a mixture of 24.5 g (0.25 mole) methylethylethynyl carbinol and 25 g (0.25 mole) vinyl-tert-butyl ether at room temperature and with constant stirring was added 0.02 ml 30% hydrochloric acid; the temperature of the reaction mixture rose to 64°. The mixture was then heated on a water bath for 5 min. at 70-75° before leaving overnight. The next day the reaction mixture was dried with potassium carbonate; 47.5 g of the product was then fractionated in vacuum from a Favorsky flask; the volatile products were trapped in a coil cooled to −7°. The following fractions were collected:

Fr. I., b.p. up to 79° (12-13 mm); 2.5 g; n_D^{20} 1.4268
Fr. II., b.p. up to 80-81° (12-13 mm); 8.5 g; n_D^{20} 1.4270
Fr. III., b.p. up to 82-89° (12-13 mm); 32.0 g; n_D^{20} 1.4286
Residue 2.0 g

In the trap was collected 1.2 g substance with the following constants; d_4^{20} 0.7720; n_D^{20} 1.3984. The constants are close to those of vinyl-tert-butyl ether.

Fraction I was not examined; it was evidently a mixture of unreacted starting compounds. Fractions II and III were combined and twice subjected to fractional crystallization to give mainly a product with b.p. 88-89° at 13 mm in the amount of 30 g or 60.6% of theory.

Examination of fraction III. The fraction had: b.p. 88-89°; d_4^{20} 0.8694; n_D^{20} 1.4290; Found MR 58.71; Calculated for $C_{11}H_{22}O_2F$ MR 58.90; Found M 193.7; 189.3; Calculated M 198.

Found %: C 72.38; 72.38; H 10.63; 10.61;
Calculated %: C 72.72; H 11.11 $C_{12}H_{22}O_2$.

The analytical data correspond to tert-butylmethylethylethynyl acetal.]

The acetal is a colorless liquid with an ethereal odor; it turns yellow when kept and gives a characteristic white precipitate with an ammoniacal solution of silver nitrate. The acetaldehyde content of the acetal was determined

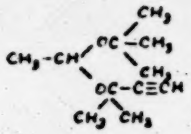
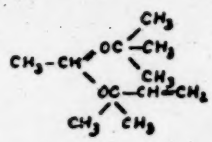
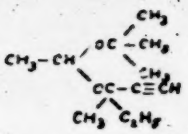
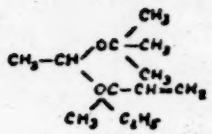
* Senior assistant Z. S. Volkova participated in the experimental work.

by the bisulfite method.

Found acetaldehyde 94, 83, 93, 72% of the theoretical.

TABLE 1

Characteristics of the prepared olefinic and acetylenic acetals

Number	Formula	B.p. in °C (p in mm mercury)	d_4^{20}	n_D^{20}	MR Found	MR Calculated	M Found	M Calculated	%C Found	%C Calculated	%H Found	%H Calculated	Yield in %
1		68-69 (16)	0.8692	1.4264	54.280	54.282	183.8 184.5	184.0	72.16 71.97	71.73	10.72 10.73	10.97	72.5
2		55 (6)	0.8532	1.4256	55.810	55.817	179.5 184.8	186.0	70.42 70.60	70.96	11.58 11.66	11.18	81.0
3		88-89 (13)	0.8694	1.4290	58.71	58.90	193.6 189.3	198.0	72.38 72.38	72.72	10.63 10.61	11.11	60.6
4		79-81 (12)	0.8540	1.4260	60.01	60.435	194.6 198.3	200.0	72.15 72.19	72.00	12.30 12.59	12.00	74.0

Reaction by the above-described procedure of vinyl-tert-butyl ether with methylethylvinyl carbinol and with dimethylethynyl- and vinyl carbinols in presence of a trace of 30% hydrochloric acid gave the corresponding acetylenic and olefinic acetals (see Table). The acetylenic acetals give a white precipitate with an ammoniacal solution of $AgNO_3$; the olefinic acetals do not give a precipitate, but they decolorize a weak solution of $KMnO_4$ and bromine water.

SUMMARY

1. A simple method is given for preparation of tertiary acetylenic and olefinic acetals containing tertiary butyl radicals; their properties are studied.

2. Dimethylethynyl(vinyl)- and methylethylethynyl(vinyl)-tert-butyl acetals were prepared.

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* T.p. = C. B. Translation pagination.

CHRONICLE

THE HUNDREDTH ANNIVERSARY OF THE BIRTH OF ACADEMICIAN N. A. MOROZOV

June 8, 1954 marked the passage of 100 years since the birth of the celebrated savant-encyclopedist and outstanding chemist, one of the earliest revolutionists, Nikolai Aleksandrovich Morozov. His memorial, executed by the sculptor Prof. G. M. Motovilov was unveiled on this day in the birthplace of N. A. Morozov, at Bork in the Yaroslav Oblast. A bronze figure of N. A. Morozov seated on a stump with a book in his hand, was erected in the park of the["Borok"] N. A. Morozov Biological Research Station of the Academy of Sciences of the USSR.

An open session of the scientific council of the biological research station preceded the unveiling of the memorial and was presided over by the Academic Secretary of the Division of Biological Sciences of the Academy of Sciences, A. I. Oparin.

The director of the biological research station, Doctor I. D. Papanin, recounted the history of the biological research station, which was organized on the initiative of N. A. Morozov, and described its routine functions which have a close bearing on the great national-economic and scientific problems of Soviet hydrobiology. The growth and the fruitful researches of the station are a worthy memorial to the distinguished scientist and loyal son of the fatherland– N. A. Morozov.

The address on the life and activity of N. A. Morozov was given by candidate of historical sciences Sh. M. Levin (Leningrad Division of the Institute of History of the Academy of Sciences USSR). He presented the main stages in the bright career of N. A. Morozov against the background of the despotic monarchical regime and the rise of the revolutionary movement. During nearly 30 years' solitary confinement in the Petropavlovsk and Shlisselburg fortresses, N. A. Morozov was able to make a profound study of various sciences and to carry out outstanding scientific researches.

Cand. Levin was followed by Acad. S. I. Volfkovich who reported on Morozov's researches in the field of natural science and in particular in chemistry. The reporter mentioned the outstanding importance of Morozov's work on "The periodic system of the structure of matter" which he wrote during many years of incarceration in the Shlisselburg fortress. In this book and in a series of other publications Morozov develops the theme of the complex structure of atoms and analyzes the basis of the periodic law of the chemical elements. He vigorously asserted the possibility of breakdown of the atom at a time when the majority of chemists regarded such a possibility as unreal and when experimental evidence for such a process was still lacking. Even at the end of the 19th century N. A. Morozov suggested that the most important problem of chemistry would by the "synthesis of elements". He considered that the chemical elements pass through an evolutionary process in the infinite development of the universe. He wrote: "What was a fantastic dream of the ancient alchemists may soon become a normal achievement of science". More than 50 years ago N. A. Morozov daringly and confidently advocated the theory of the complex structure of atoms, of the transmutability of elements, of the artificial preparation of radioactive elements, of the unusual stores of intraatomic energy. Reviving an idea of Dumas, N. A. Morozov advanced a periodic system of organic compounds ("carbohydride" radicals). At the start of the 20th century Morozov proposed the hypothesis that new stars are born by explosion of old stars due to decomposition of atoms of radioactive matter. Today this previously controversial hypothesis is accepted in slightly modified form by wide circles of astronomers and physicists.

S. I. Volfkovich later drew attention to a series of other notable ideas and discoveries of Morozov in various fields of science and indicated the need for deep and many-sided study of the rich literary works of Morozov.

The final speaker was Academician A. I. Oparin who pointed to the great importance of the studies in progress at the N. A. Morozov "Borok" Biological Research Station on hydrobiology, ichthyology, ornithology, hydrochemistry and other sciences. These researches are of importance not only locally but for the Union in general, particularly for clarification of the problems associated with the tremendous hydrotechnical developments in the USSR.

At the conclusion of the open session of the scientific council, at which were present Moscow representatives of the Academy of Sciences of the USSR, of societies from the oblasts and raions, as well as delegates of the Leningrad scientific institutes at which Morozov worked, the memorial was unveiled. The memorial commissioned by the Presidium of the Academy of Sciences was unveiled by Academician A. I. Oparin.

At the foot of the memorial were placed wreaths from the Presidium of the Academy of Sciences of the USSR, from the Division of Chemical Sciences of the Academy of Sciences of the USSR, from the "Borok" Biological Research Station, from the Leningrad V. F. Lesgaft Institute, and others. Also present at the unveiling of the memorial were representatives of local [illegible].